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DEVELOPMENT OF ANALYTICAL METHODS FOR TRACE
ELEMENTS IN COAL USING OPTICAL
EMISSION SPECTROSCOPY

by



ARTHUR BOLLO-KAMARA

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled DEVELOPMENT OF ANALYTICAL METHODS FOR TRACE ELEMENTS IN COAL USING OPTICAL EMISSION SPECTROSCOPY submitted by ARTHUR BOLLO-KAMARA in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

The determination of trace elements in coal has been of considerable interest for various reasons, such as their use for seam correlation, their influence on coal properties, their potential use as a source of rare elements and presently of more concern their association with certain detrimental effects during coal utilization, like poisoning by some trace elements of the costly catalysts in certain of the proposed coal gasification and liquification schemes, and the release of potentially toxic volatile materials into the atmosphere and the surroundings during combustion and disposal of the coal ash left after combustion.

Optical emission spectroscopy was used in the determination of the trace elements in some Alberta coal. A quantitative method was developed using dc-arc as the excitation source and a spectrograph with photographic detection as the signal processor. The precision of the excitation source was examined. The inductively coupled plasma (ICP), which has similar multielement analysis capabilities, was used as a comparison source for the dc-arc and also in a preliminary study to investigate the potential of the "analytical power" of the ICP when it is used with a spectrograph. A precision study was also done with the ICP and the results compared to that of the dc-arc.

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CHAPTER I

Introduction

It all started millions of years ago, when the sunshine and chlorophyll transformed the hydrogen, oxygen and carbon of the air and soil into cellulose and lignin, which later became the complex chemical coal. Usually we can predict the fate of carbon complexes in nature as a gradual degradation to simpler compounds, ultimately to carbon dioxide. Carbon in the form of coal, an organic substance, is a biological and geological accident (1), resulting from minor inefficiencies in the microbiology and biochemistry of the carbon cycle. There seems to have been an imbalance in the continual flow of energy into and out of this cycle almost achieving a state of balance with respect to carbon compounds. The slight imbalance is of sufficient magnitude as to result during geologic time, in the accumulation of the sedimentary deposits approximately known as fossil fuels and which inevitably includes coal.

Most scientists have attributed the degradative alteration of plant residues mainly to the unceasing activities of innumerable microorganism, chiefly fungi and bacteria, but also including certain forms of unicellular animals and protozoa. These organisms have developed during the course of their evolution and natural selection, many varied complex enzymic systems, which are specifically adapted to the breakdown of the organic complexes in plant tissues. The activities of these pervasive array of parasitic and

saprophytic agents is normally limited only by the supply of organic matter available for metabolism. Under some environmental adversities microbiological processes are retarded and eventually arrested. At this stage, then, the accumulative phase far exceeds the degradative phase and organic sedimentation or rather coal formation results.

A. MINERAL MATTER IN COAL

The mineral matter in coal also known as the ash content has been reported to have five modes of occurrence:

- 1) impurities of rare and trace elements.
- 2) disseminated crystalline mineral matter.
- 3) detritol mineral matter.
- 4) crystalline mineral matter in fractures, veinlets, petrification and nodular masses.
- 5) bonded impurities.

This mineral matter that is obtained when coal is ashed has been classed by some workers as impurities that are quantitatively unimportant, uncommon, rare and trace elements of coal (2). Although the inorganic content of coal has been classed as a troublesome residue, it has been used as an important point of information, useful in predicting the amount of ash in coal, the characteristic of the coal, and improvements that can be expected from coal cleaning.

Chatterjee et al. (3) have used trace element studies to correlate seams of South Wales coal in Australia. It is also of relevance to know the species of minerals present,

the range of particle or crystal size and the distribution in the coal. It is also important to note at this point that the mineral matter of coal may not always be termed as an objectionable feature, since it has been proposed by some workers as a source for the recovery of certain rare elements that are in great demand, e.g. germanium, vanadium and molybdenum to name a few (4,5).

For an analysis of trace elements in coal it is rather fundamental to consider in more detail the occurrence of mineral matter in coal.

1. Impurities of Rare and Trace Elements

What is termed as the impurities or rare and trace elements are generally regarded as those elements that are intimately associated with the organic matter and probably represent at least an inherited characteristic from the plant stage of coal formation. Growing plants, as we know, selectively or rather preferentially absorb and concentrate a number of elements in their tissues, e.g. magnesium in the porphyrin ring of chlorophyll. Plants also take up and store crystalline chemical substances such as silicates, carbonates and oxalates. Because there are thousands of species in the flora of the prehistoric time, it is obvious that the assemblage of trace elements is not the same for all coals, but nevertheless the total number found in any particular coal ash is usually very large. Not all of

these rare and trace elements of coal are associated with the inherent organic component of coal. Goldschmidt (6), investigating the unusual concentration of germanium in coal ash suggested that this occurrence should not be solely described as selective absorption by plant tissues during growth. It has been advocated and discussed in great detail by Fortescue et al. (7), that organic matter of coal may absorb the element from water or gaseous solutions that enter the coal during later stages of metamorphic developments. The report also suggests that the source of germanium bearing waters or gases was the rock strata overlying or underlying the coal beds. The absorption of germanium by the organic matter occurred at the top and/or the bottom of the coal bed.

2. Disseminated Crystalline Mineral Matter

Disseminated crystalline mineral matter are usually well formed mineral crystals that are observable with a microscope under high power. Pyrite is reported to occur most frequently and it is believed that aqueous solutions containing iron salts enter the plant substance during the peat stage, when the parent material of coal is in a state of water saturation.

3. Detrital Mineral Matter

Detrital mineral matter is always intermixed with attritus and usually has the characteristics of fine

sand silt and clay. Their origin is due to weathered and eroded rock and its residual product soils. Sediment, which is the mineral debris from this source when water is transported, and atmospheric dust, when air borne, must have been deposited into coal forming swamps developed in shallow basins along low-lying coastal plains.

4. Crystalline Mineral Matter in Fractures

The burial of peat under sedimentary cover causes comprehensive forces to be exerted upon the water saturated plant debris and as the huge volume of water is slowly expelled there is considerable shrinkage in the deposit. The shrinkage bed is marked by development of nearly vertically aligned tension fractures. These fractures make it possible for water to move freely through the bed. Usually such water in the coal bed contains minerals in solution that under favorable conditions are precipitated out of the solution, filling the fractures with crystalline mineral matter. Coals with these fractures usually break into large lumps exposing thin sheets of mineral matter on the vertical surfaces of the coals. It seems evident that such crystalline matter would be responsible for the unusually high ash content encountered in some coals.

5. Bonded Impurities

Bonded impurities which result from layers of inorganic matter interbedded with the coal are usually thin and

even difficult to distinguish from the dull layer of coal. Such layers of impurities that are usually conspicuous and easily measured are called "portings" by miners, and are sometimes used as horizontal markings.

Usually the last three described types of mineral matter in coal can be removed by crushing to free the minerals from the coal followed by gravity separations. The disseminated crystalline minerals and the dispersed detrital mineral grains can be freed only by crushing coal to extremely fine size.

From the above, it is apparent that there is an unpredictable abundance of elements in coal whose distribution one way or another has been dictated by nature.

B. WHY STUDY TRACE ELEMENTS OR THE MINERAL MATTER IN COAL

All living organisms are exceedingly sensitive to external stimuli. Such stimuli add on undesirable stress to functioning cells. As most effects of environmental stimuli are not immediately obvious to man, we are generally not aware of physiological changes which might occur to maintain internal stability. Despite the incomplete knowledge of effects of air pollution on humans, priority of human health protection must override the lack of absolute proof, hence warranting the need for a study of trace elements in coal.

The annual world coal consumption approaches 3×10^9 tons. On combustion of this coal the trace elements in coal

are transferred to slag, fly ash, or gases and are discharged to the environment. It is this discharge of trace elements that has been of concern to environmentalists and chemists alike.

There are many reports in the literature on trace elements in coal, but unfortunately, there is no comprehensive report on coal in Canada, or to be more specific coal in Alberta. There are a few scattered reports in the literature on the presence of germanium and other trace elements in Western Canada coals (2,7). To understand and appreciate a study on trace elements in coal it is important to review some of the studies that have been done on coal. Bertine and Goldberth (8) have shown that the total quantities of trace elements involved in coal combustion are large, being roughly comparable to the quantities annually mobilized by the natural process of weathering of crystal rock. They also propose that about 5% of the mineral content of coal is discharged to the atmosphere and selective volatilization leads to greater atmospheric discharge for arsenic, silver, cadmium, tin, antimony, lead, zinc, tellerium, mercury and bismuth.

Increased potential health risks are now associated with those elements which are highly volatilize and with those discharged principally as submicron particulates (9). In a discussion by Schultz et al. (10), they suggest that it is possible to remove over half of the potentially toxic

trace elements present in coal when the mineral matter is reduced during coal washing, also they report that when coal is burned in a power plant, about 13% of the Hg (mercury) and about 50% of the Pb (Lead) and Cd (Cadmium) may remain with the fly ash. Hence pretreatment may lessen the amount of toxic element discharged to the atmosphere when coal is burned in power plants.

Hall, Varga, and Magee (11), in their discussion on trace elements and potential pollutant effects in fossil fuel, proposed that the amounts of trace elements found in coal are for the most part close to their average crustal abundance, and hence are not toxic at this level. Because of the extensive variation of trace elements in coal, they suggested that the potential danger from toxic elements such as Hg (Mercury) in coal was often overstated by averaging results. For the volatile elements which are considered most hazardous, that is F, As, Se, Cd, and Pb, the available analytical data was spotty and unreliable; but nevertheless the long term accumulative effects are what we are more concerned about.

The trend in Alberta now is towards coal combustion; the reason for this trend is quite evident from the high cost of natural gas and oil. To this date very little has been done with regards to a study of the distribution, or occurrence of trace elements in coal. The present one-time harvest of petroleum and natural gas will inevitably come to

an end and coal will be an important source of energy. In the province of Alberta the Government has shown increasing interest in coal research, their latest move is the proposed construction of a coal research laboratory in Devon (12).

Many of the coal mines around the world have been extensively studied but the reports that are of considerable interest to us are the reports from the Illinois Geological Surveys (13). In these reports 25 coals mainly from the Illinois area were analyzed using about six different methods. The estimates of trace elements determined by the different methods are well documented in the report. Another report that documents the occurrence of trace elements in coal is a report by Swane (14), on trace elements in New South Wales coals. These two reports are quite extensive and contain several references on different elements, their occurrence in the organic or inorganic part of coal, and discussions on the usefulness of trace elements found in coal.

A variety of methods have been used in analysing coal for trace metals. Kahn et. al. (13,15) used x-ray fluorescence. The precision reported ranges from $\pm 1\%$ to $\pm 15\%$. They report that because coal is mainly composed of light elements its matrix is well suited for almost interference free x-ray fluorescence, but it should be pointed out that x-ray fluorescence is not a very sensitive technique. Photon

activation analysis has also been used by Zoller (16) to measure concentrations of trace elements in the submicrogram ranges in atmospheric particulates, and suggest that the technique is applicable to coal. Brown et al. (17) and Sharkey et al. (18) have reported using Spark Source Mass Spectroscopy in the determination of trace elements in coal, fly ash, miners lung tissue, respirable coal dust and particulate matter. Optical emission spectroscopy (D.C. arc) has been used for the analysis of coal (13). Because coal is a solid, atomic absorption analysis has resulted in the development of wet digestion methods (19,20,21). Bailey (22) analysed coal ash for trace elements by solvent extraction followed by atomic absorption spectroscopy. Using methyl isobutyl ketone and dimethylglyoxime for nickel and methyl isobutyl ketone and ammonium pyrrolidine dithiocarbamate for lead he found improved results over those obtained by direct aspiration of the digested solution. Neutron Activation Analysis has been one of the most widely used methods for analyzing trace elements in coal, the reason being that it is a highly sensitive, nondestructive multielement technique. The method was extensively used in the Allen Steam plant study by Lyon and Emery (23). Sheibley (24) applied the method for routine analysis of 1000 samples per year, and a complete trace element analysis of 20-24 samples per week averaging 3-3.5 man hours per sample. Block et al. (25) also report using neutron activation analysis for the

measurement of over 40 elements in coal. A systematic comparison of thermal and epithermal irradiations in the instrumental activation analysis of coal and fly ash was carried out by Rowe and Steinners (26); from a total of 44 elements they found the epithermal irradiation technique advantageous for 20 elements.

Murphy (27) used peroxide digestion to oxidise coal samples prior to Hg determination by cold vapour atomic absorption. Although the method seems suitable for the determination of the very volatile elements, it is both time consuming and dangerous.

From the above discussions it is evident that a variety of analytical methods are applicable to the analysis of coal for trace elements; because of the unpredictable distribution of elements in coal no one report can serve as a model for the kind or type of elements found in coal. The trace element contents differ from basin to basin in various deposits, and in different seams.

C. D.C. ARC OPTICAL EMISSION SPECTROSCOPY

In this study a continuous dc arc discharge is used as the primary excitation source for the analysis of coal. This dc discharge is usually maintained between carbon electrodes. The continuous dc discharge is produced in a circuit containing a dc power source, providing 220 to 250 v with a ballast resistance connected in series with the analytical gap. The discharge is initiated by

momentarily bringing the electrodes into contact with each other. The basic electrical parameters of the discharge are the current strength and the voltage drop across the gap. Extensive discussions on the variables that affect these parameters are detailed by Boumans (30).

The dc arc source can be used for qualitative analysis with quantitative estimates, semi-quantitative and full quantitative analysis. In brief these analytical procedures can be described as follows:

1. Qualitative Analysis

Basically it involves identifying all spectrographically detectable elements in a sample, which would involve confirming the presence of the most sensitive lines of an element. This procedure can be used for identifying elements or comparing two samples to see if there is any difference. The procedure seems basic and simple but reading a film properly for qualitative identification can be more difficult than analyzing a film in a routine quantitative procedure. It usually requires the expertise of an experienced spectrographer who is familiar with the spectra of common elements and who can recognise the possibility of interfering lines. He must be familiar with specifications for various materials so as to be able to pay special attention to those elements that may be critical at the trace level. Moreover he must be familiar with the spectra of the elements in different base matrices, and he should have wide experience in observing

the effects of varying major constituents. Usually the analytical conditions are optimised to obtain maximum resolution, this would include a small slit width and the use of a high resolution grating spectrograph.

2. Qualitative with Quantitative Estimates

This procedure is essentially the same as that described above with the exception of establishing to some extent the amount of elements present. The order of magnitude of the estimates is seldom numerical, they are most often reported as major, minor, and trace depending on the extent of blackness on the photographic film. Also since some understanding of the lower limit of detection for most elements is known, that is about 1 ppm, the absence of an analytical line of interest thus indicates that the element of interest is less than 1 ppm. This type of analysis is mostly used in survey analysis to obtain a crude estimate of the abundance of elements in a sample.

3. Semi-quantitative Analysis

This procedure is more tedious than the latter in that it involves the controlling of different parameters in arcing and in some cases the treatment of data. The results are usually reported in numerical form as percentages. Usually sets of standards are arced with the sample. These standards are chosen depending on the kind of results required. For example, standards could be used that have concentrations of 0.1%, 0.01%, 0.001%, to 0.0001%; or in some cases 0.1%, 0.03%,

0.01%, 0.003%, 0.001%, 0.0003%, 0.0001%. Both sets of standards can be easily prepared or obtained as Spex spectrochemical G standards. The Spex standards contain 49 elements diluted 1:1 by weight with graphite. The samples to be analysed are usually diluted 1:1, 1:10, and in some cases 1:100 by weight with graphite. Usually no internal standard is used, but Harvey (32) has developed a semi-quantitative method that uses background as the internal standard. The background that is measured is actually the incandescence from the electrodes. For reproducibility the samples and standards are weighed into the electrode. The photographic density is measured from the densitometer. The precision of this method is usually poor, being about 20% to 50%.

In many instances this procedure is adequate to provide the necessary information required, especially when time and the amount of sample preclude a quantitative method. Furthermore it can be utilised in establishing quantitative methods, especially where standards are to be prepared, since it gives the spectrographer the necessary information as to which elements are present and their approximate concentration. This would help establish an initial level for the standards.

4. Full Quantitative Analysis

Before a full quantitative method is developed, it is essential to know the nature of the sample, its major constituents and arcing characteristics of the elements to be analysed. This information is important when an internal

standard is to be added to the standard and the samples. The standards are usually prepared so that they match the samples as closely as possible. The transmittance of spectral lines are read from the densitometer. These transmittance values are somehow related to the intensity of the light striking the emulsion in the spectrograph, the developing process, and the characteristics of the emulsion itself. The relationship is not very simple, since it involves complicated mathematical expressions. However, the light intensity as related to the film blackening or the density is determined empirically by calibrating the emulsion, which sometimes involves highly controlled quantitative analysis for each batch of emulsion. Detailed descriptions of calibrating emulsions will be discussed under quantitative analysis.

As is evident from the above discussion full quantitative analysis is more tedious and requires more work. The reproducibility is quite good, with a 5% to 10% precision. Finally extensive discussions on the fundamental steps to be considered in developing a full quantitative method are detailed in Harvey (32).

The main objective of this project was to develop an analytical method for the determination of trace elements in coal. Qualitative and semi-quantitative analytical methods were developed. A quantitative analytical method was developed involving development of standards with the same matrix as the sample. A simple program to facilitate quick

and easy emulsion calibration for the photographic plate was developed for a pocket calculator. For comparison purposes a survey study was also carried out substituting the dc arc source with an inductively coupled plasma. The precision of the dc arc source was compared with that of the ICP.

CHAPTER II

Sample Preparation

All eighteen samples were obtained from the Energy Resources Conservation Board (28). They were obtained from mines around Alberta; a catalogue of the samples obtained is shown in Table I. There is no detailed information as to how the sampling was carried out. The general description of the eighteen samples can be summarised as small pieces to big chunks in terms of physical size and dull grey with brownish-yellow specks to jet black in terms of color. Other samples that were used in this study are the NBS coal sample and the NBS fly ash. These samples were obtained from the National Bureau of Standards of the United States of America. The samples contain certified values of different elements. They were used extensively as reference materials for calibration of instruments used and optimization of methods developed.

Since our main objective was to develop a routine analytical method for trace element determination, no particularly rigorous routine was used in obtaining a portion of the samples for analysis.

A. GRINDING

From a single container big chunks were broken down to smaller pieces with a hand grinder and mixed thoroughly, then smaller portions were taken at random as a representative of the total sample. Two methods were used to obtain

TABLE I
Coal Sample Catalogue

<u>Sample No.</u>	<u>Origin</u>
1	High vale mine south pit, No. 2 seam virgin coal, 11 feet thick.
2	High vale mine west pit, No. 1 seam (two days hard cut).
3	High vale mine west pit, No. 2 seam virgin coal.
4	High vale mine west pit, No. 3 & 4 seams.
5	Cardinal river coal, 50 A1 pit. (1975)
6	Cardinal river coal, 50 B1 Pit. (1975)
7	Incarray fresh coal unoxidized.
8	Wilson seam.
9	Riverside mine.
10	McIntyre mines, No. 2 and No. 4 seams.
11	McIntyre mines, No. 11 seam.
12	Tent No. 4 pit fresh coal.
13	Tent No. 2 pit.
14	Vesta mine No. 2
15.	Diplomat mine 7400 pit.
16	Diplomat mine 992 pit.
17	Vesta mine No. 1
18	Star Key mine.

fine particles of uniform size. In the first method the samples were ground in an electric grinder with metal sieve to obtain very fine coal powder, that would go through at least 200 mesh. Extreme care was taken not to contaminate the samples, this included cleaning the grinding parts of the grinder very carefully after grinding each sample, and "dry cleaning" the container funnel of the grinder by grinding a small portion of the new sample for a few minutes and then discarding. In the second method a Spex 8000 mixer/mill was used.

B. ASHING

Because of the organic nature of coal and its overall chemical composition, whole coal cannot be conveniently analysed using dc arc emission spectrochemical techniques; hence the mineral matter of coal must be obtained by oxidizing whole coal to its mineral oxides. Low temperature ashing (L.T.A.) and high temperature ashing (H.T.A.) are usually the two main techniques used with the latter being the most widely used.

Low temperature ashing, also identified as electronic low temperature ashing or radio-frequency ashing, is a technique in which oxygen is passed through a high energy electromagnetic field produced by a radio-frequency oscillator. Usually the oscillator tube is operated at 13.56 MHz. As the oxygen is passed through the radio-frequency field, a discharge takes place. The activated gas plasma is

usually a mixture of atomic and ionic species as well as electronically and vibrationally excited states. The activated oxygen passes over the coal sample, and oxidation of the organic matter takes place at relatively low temperatures. By using this technique it has been reported that the major constituents of coal; pyrite, kaolinite, illite, quartz and calcite, are considered to be unaffected by the radio-frequency ashing technique (13). Most trace elements contained in the coal in inorganic combination are not volatilized during low temperature ashing, also many of the elements thought to be present in organic combination also remain in the low temperature ash. Thus the main advantage of L.T.A. is the retention of volatile elements that are usually lost when high temperatures are used for ashing. One major disadvantage of L.T.A. is the time involved. The ashing of a few grams of coal can take up to 24 hours to complete. It has also been shown that low temperature ash is generally unsatisfactory for the determination of the less volatile trace elements by optical emission spectroscopy because the ash sample contains chemical compounds that behave erratically in the dc arc (13).

High temperature ashing involves ashing coal in a muffle furnace at temperatures around 500 to 600°C. Although most of the volatile elements are lost at such high temperatures the ash is in a form that is quite suitable for arcing, since those remaining are mostly in the oxide form.

In this analysis the high temperature ashing technique was employed; triplicate portions of each coal sample were accurately weighed in a porcelain crucible, and placed in a conventional muffle furnace where the temperature was gradually increased to 600°C within a period of three hours. Intermittent stirring at two hour intervals was done with a platinum wire. The percentage ash in each sample was determined by taking an average of the three portions of each coal sample, the three portions are carefully mixed to form a representative ash for each of the eighteen coal samples. The ashed samples are allowed to cool down to room temperature in a desiccator, and weighed at constant time intervals after reheating to obtain a constant weight. The weighed portions of each sample are then combined, ground in an agate mortar and a spex mixer/mill to a fine powder, crushing small sand and clay particles, and finally dried in an oven at 120°C overnight. Although it had been stated earlier that the ashing temperature is 600°C, it would be more accurate to state that the temperature varied between 500°C and 600°C, and the average time of ashing was between 5 to 6 hours. Table II shows the percentage ash for each sample, and Table III shows a grouping of the samples with regards to their percentage ash. The average percent ash within samples is relatively the same. In all eighteen samples the average percent ash was 15.6. From Table III it is apparent that nine of the coal samples yield percentage

ash values below 10% while five fall between 10% and 20%; hence 77% of the eighteen coal samples contain between 1 to 20% ash. Note that samples (4) and (12) show high ash content. Recalling from Chapter I on the occurrence of mineral matter in coal it could be realised that this high ash content is not very abnormal, since it is possible to have a considerable amount of mineral matter associated with coal deposits.

No work was done on the determination of the very volatile elements which are lost during high temperature ashing. Since the method used in ashing is analogous to that of Ruch (13), most of the very volatile elements lost during ashing would be very identical to those reported in Table IV. From this table it is clear that it would be impossible to retain Hg, Br, Sb or F at the ashing temperature used, but almost all of the others which are potentially volatile will be retained at the ashing temperature used.

TABLE II

Percentage Ash in Coal Samples

<u>Sample</u>	<u>% Ash</u>	<u>% Relative Standard Deviation</u>
1	11.6	6.2
2	22.7	8.4
3	15.7	4.1
4	48.8	1.3
5	22.4	6.0
6	9.0	0.6
7	16.2	9.5
8	3.3	2.9
9	5.8	7.5
10	11.0	3.6
11	6.1	4.9
12	60.4	1.8
13	5.8	0.8
14	5.5	17.7
15	9.8	12.5
16	12.3	0.9
17	7.4	1.6
18	6.5	1.0
NBS	13.5	0.2

TABLE III

Grouping of Samples According to Percent Ash

<u>% Range</u>	<u>Sample</u>	<u>No. of Samples</u>
1 - 10	6, 8, 9, 11, 13, 14, 15, 17, 18	9
10 - 20	1, 3, 7, 10, 16	6
20 - 30	2, 5	2
30 - 40	--	-
40 - 50	4	1
50 - 60	12	1

* NBS Coal % Ash = 13.5%

TABLE IV
Volatility of Trace Elements in Coal

Low temp. ash elements lost	Low temp. ash elements retained	High temp. ash +
Hg up to 90%	Ga. Cu*	Be
	Se Pb*	Ge
Br up to 100%	As V*	Mo
	Zn* Mn*	B
Sb up to 50%	Ni* Cr*	
	Co*	

F

* Also retained in ash prepared at 450°C.

+ No significant losses observed in coal ash prepared at 300°C to 700°C.

from Ruch et al. (13).

CHAPTER III

DC Arc Qualitative Analysis

Optical emission spectroscopy was used in the analysis; the source for volatilizing the sample and exciting atomic species was the direct current arc. Detailed descriptions of the physical characteristics of the dc arc are well documented in the following references; Ahrens and Taylor (29) and Boumans (30).

A. INSTRUMENTATION

The instrumentation can be summarized as follows.

1. Power Supply

A Jarrel-Ash utility dc arc power supply with a 230v, 60Hzs supply was used. Power is supplied to the electrodes with this power supply with an output voltage of 208v dc and an adjustable current of 3-20 amps. The current is set using the row of five toggle switches in the front panel. The residual current is 3 amps (all switches down) and increasing current levels can be obtained by setting the appropriate switches. Also in the front panel are a current meter, fan switch and a stop-start switch.

2. Arc-Spark Stand

Generally for analytical spectroscopy it is necessary to have the arc excitation stand rigidly mounted on an optical bench. The need for improved accuracy and precision has resulted in the development of versatile enclosed units for

excitation of analytical samples. Spex industries arc/spark stand #9010 was used. The arc stand is an enclosed system constructed so that fumes and volatile substances enter an exhaust system and are withdrawn from the laboratory. The door of the arc stand has safety interlocks and all electrical connections are shielded. Electrodes can be positioned laterally and horizontally by external means, and electrical, gas, air and water facilities are available within the excitation enclosure. Also the enclosed system provides the capability of igniting the arc in an inert atmosphere and a controlled atmosphere. This facility is utilized in the quantitative analysis.

3. Dual Grating Spectrograph with Dual Illuminator Accessory

Since spectrography deals with photographic recording of a spectrum, it is essential to have a dispersing device (grating), which separates the light produced by the volatilized elements into its component wavelengths. This spectrum is then recorded on a photographic plate.

The Bausch and Lomb (B & L) Dual Grating Spectrograph is a compact instrument that offers a wide range of techniques, speedy and efficient operation, and high resolution and dispersion. In general the efficiency of any spectrograph is the sum of all its mechanical and optical components, but the heart of the instrument is the grating. There are two gratings in the spectrograph which operate independently, the desired wavelength area from each for a specific analysis

is selected at the instrument panel with simple dial controls. Easy-to-read duplicate scales show the range and the spread at a glance.

The dual grating has a relatively flat field. The plate curvature is slight, reducing risk of plate breakage. It is designed to hold one 4" × 10", one 2" × 10", or two 2" × 10" glass plates. Mechanical occluders for each grating are controlled by knobs on the instrument panel. Either knob may be set open when it is desired to use one grating only. In most cases separation of spectra is desired, and this is achieved by setting a dial on the instrument panel to permit spectra to be photographed one above the other on the same plate, separated by a space of up to 50 mm.

The use of two gratings provides greater flexibility of dispersion. One grating, with 600 grooves/mm, has a dispersion of 8A/mm, first order, and 4A/mm second order; the other, with 1200 grooves/mm gives 4A/mm first order and 2A/mm second order. These two dispersion ranges give both the low dispersion necessary for recording of a complete spectrum and the high dispersion required for critical study of a complex range of that spectrum with one exposure. The ranges desired are easily dialed from the instrument panel.

Four slit widths are provided (10, 20, 50 and 1000 microns). To permit quick, convenient selection of slit cover lenses and filters, a turret with 8 apertures is provided. This is where the two step filters are inserted for full quantitative analysis.

The unique use of two gratings in the Dual Grating Spectrograph calls for an illuminating system that will provide an image of the source for each grating; the dual illuminator is a simple enclosed unit which clamps to the accessory bed. All routine adjustments are made externally with two controls including provision for gap scanning in cathode and anode layer work, and also for alignment of electrodes, so that the image is centered on the photographic plate. A filter turret allows moderating the light for each grating. Two source images, one for each grating, are created by the achromatic optical system consisting of a series of mirrors. Each of the images is focused on its respective grating by a field lens (146 mm f.l.) in the slit holder. Because the lower resolution grating is actually blazed for the visible, most of the analytical lines reported were determined with the high resolution grating.

4. Electrodes

High purity normal density (HPND) graphite electrodes are used. The lower electrode (anode), which also is the sample electrode is the necked crater type with a diameter of 3/16" and a crater depth of 3/16". The ASTM number is 513. These electrodes classed as the semiquantitative type; basically have a hole drilled in the centre of a graphite rod of a suitable diameter to accommodate an amount of sample ranging from 50 to 100 mg. The electrodes are usually machined to specified dimensions so that they are all of

uniform size.

The advantage in using this kind of electrode, is the fact that having the undercut on the lower electrode facilitates higher electrode temperatures to be maintained with the consequences of easier vaporization of the more refractory materials.

The counter electrode (cathode) is the pointed type 4039 with a diameter of about 3/16". The advantage of using this type of counter electrode lies in the fact that the arc discharge on the electrode centres well as long as samples do not contain too high a percentage of alkali or alkaline earths, in which case condensation on the upper electrode occurs, causing the arc to wander from side to side. A disadvantage in this type of counter electrode is the fact that it lacks an undercut which usually prevents excessive wandering of the arc and also minimizes the conduction of heat to the body of the electrode, thus restricting carbon vaporization to the tip of the electrode. This point is rather important since background contributed by electrode vaporization is of considerable concern when long exposures are taken.

B. QUALITATIVE ANALYSIS

The ashed coal samples were diluted with graphite, in a 1:1, 1:5 and 1:10 ratio, that is 1 part sample to 1 part graphite by weight. The 1:1 dilution usually caused the sample to boil out of the electrode while the 1:10 dilution

resulted in a loss of sensitivity. The 1:5 dilution proved quite suitable and was used in all the dilutions for qualitative analysis. The iron spectrum is used for calibration. The arcing conditions used are shown in Table V. Since the spectrograph is a dual grating spectrograph, two wavelength ranges were used, 240.0 nm to 340.0 nm and 240.0 nm to 440.0 nm. For all qualitative analysis the following settings were made on the spectrograph:

Slit width - 10 nm

Slit height - 1.5 mm

Plate drive - 1.5 mm/step

As can be seen from Table V the two filters used for the two gratings were set at different transmittance since this was found to be the optimum condition for obtaining a clear spectrum of samples arced.

For all spectrographic work, 4 × 10 inch Kodak spectroscopic plates, type 1a were used (Catalogue #156 7387). These plates have a high contrast compared to other emulsion types and are the best for emission spectroscopy. Darkroom parameters used in developing photographic plates are shown in Table VI. All eighteen coal samples were arced under the conditions specified in Table V, and the photographic plate developed under the conditions listed in Table VI.

A Spex master plate coupled with a Jarrell-Ash 21-000 non-recording microphotometer were used as a comparator densitometer in identifying elements. Most of the elements

TABLE V

Arcing Conditions for Qualitative Analysis

Sample	Filter (1,2) (%)	Current (amps)	Anal. Gap (mm)	Exposure Time (secs)
Fe	100,100	4	4	15
1 → 13	25, 6	12	4	90
13 → 18	25, 6	12	4	120

Note: Sample 13 → 18 arced with different electrodes, resulting in longer exposure.

TABLE VI

Dark Room Parameters

Kodak Developer	D-19 for 2 min.
Stop bath	20 - 30 secs
Fixer	Rapid fix for 2 min.
Washing	Cold water 10 - 15 min.
Drying	> 1 hour (air dry)

reported were detected with the 240.0 - 340.0 nm grating which is the higher resolution grating. The other grating has a lower sensitivity because it is blazed for the visible. It usually covers the 240.0 nm to 440.0 nm region. Because of strong cyanogen band emission, and the poor sensitivity in the ultraviolet it was seldom used except in a few instances for confirmation purposes. The optimum conditions for arcing parameters were arrived at after many tries (see Table V). A summary of the qualitative analysis is shown in Table VII. The intensity of the lines of elements are subjectively reported as S (strong), VS (very strong), M (medium), W (weak), Tr (trace). Twenty-five elements were detected. An element reported as not detected implies that the most persistent line is absent and the element is below the detection limit of the excitation conditions and the detector, typically about 1 ppm for most elements. From the data available it is clear that the major elements in the coal ash are aluminium, calcium, iron, magnesium, silicon and titanium. This assignment was done on an approximate concentration scale, such that all elements greater than about 1 percent are classed as major constituents. All others could be classed as minor or trace components. Since this distribution is done rather subjectively from the spectrum obtained for qualitative analysis, all other elements that are not listed above as major constituents are trace. The concentration of the trace elements

TABLE VII		Qualitative Results (elements detected)																	
Element/Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Wavelength (nm)
Ag Silver	T	T	T	T	T	T	T	T	T	M	T	T	T	M	M	M	M	M	328.0, 338.3
Al Aluminium	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	308.2, 309.3
B Boron	S	S	S	S	S	S	T	S	S	S	W	ND	S	M	M	M	M	M	249.6, 249.7
Ba Barium	S	S	S	S	S	S	W	S	T	S	T	T	W	M	M	M	M	M	307.2
Be Beryllium	W	W	W	W	W	W	W	W	W	W	W	W	W	S	M	M	M	M	313.0, 313.1
Ca Calcium	S	S	S	W	W	W	W	S	W	S	W	T	S	S	S	S	S	S	317.9, 315.9
Co Cobalt	S	S	S	S	S	S	S	S	S	S	S	S	S	CN	CN	CN	CN	CN	340.5
Cr Chromium	W	W	W	S	S	W	M	W	M	S	W	M	S	W	W	W	W	W	284.3, 425.4
Cu Copper	S	S	S	S	S	S	S	S	S	S	S	S	S	T	T	T	T	T	324.7, 327.3
Fe Iron	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	311.0 (standard ref.)
Ga Gallium	M	M	M	M	M	M	M	M	M	M	M	M	M	O	O	O	O	O	294.4
Ge Germanium	ND	ND	ND	ND	ND	ND	ND	ND	ND	W	ND	ND	ND	ND	ND	ND	ND	ND	265.1, 326.9
Hf Hafnium	S	S	S	S	S	S	S	S	S	S	S	S	S	S	ND	ND	ND	ND	307.2
Ir Iridium	M	W	W	S	S	W	W	M	S	W	M	S	W	W	ND	ND	ND	ND	284.9
Mg magnesium	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	377.9, 285.2
Na Sodium	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	330.23, 330.29
Ni Nickel	W	W	W	T	W	W	W	W	T	W	T	W	W	CN	CN	CN	CN	CN	305.0, 141.4
Pb Lead	M	M	M	M	M	M	M	M	M	M	M	M	M	M	W	S	W	S	283.3, 280.2
Si Silicon	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	250.7, 388.2
Sn Tin	S	W	W	W	W	W	W	T	W	W	T	T	W	O	O	O	O	O	317.5, 283.9
Ti Titanium	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	334.1, 336.1
V, Vanadium	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	318.3, 318.9
Zn Zinc	S	S	S	W	S	S	S	W	S	S	W	S	S	S	S	S	S	S	328.2

CN - Cyanogen Band
M - Medium
ND - Not Detected
O - Overlap
S - Strong
T - Trace
VS - Very Strong
25 Elements

varies from sample to sample. For example germanium was only detected in sample 11. This confirms the report cited earlier about the occurrence of germanium in some Western Canadian coals (7).

These qualitative results are similar to those reported by other analysts in different parts of the world. The only major difference being that some reports show rare trace elements that are peculiar to the coal sample analyzed ; for example gold and uranium in References 13 and 14.

C. TIME STUDY

Selective volatilization is one of the most characteristic phenomena of the dc arc. Some elements distill almost completely before others begin to volatilize. This is an important point to consider when quantitative analysis is to be done. For a sample like coal with many elements it is important to know as completely as possible the selective volatilization characteristic of the sample. This was done by carrying out a time study using the moving plate technique, in which the spectrograph plate holder is racked stepwise at definite intervals of 10 secs.

Time studies not only give information as regards the distillation of elements in the arc plasma, but also are an integral step in the development and implementation of dc arc spectrochemical analyses. Without a knowledge of this time behavior it is next to impossible to set up meaningful exposure times or even determine internal standard line

compatibility (29,39).

A time study was carried out on coal sample ash #3, National Bureau of Standards (NBS) coal ash and NBS fly ash. The arcing conditions for the time studies are listed in Table VIII. All samples were diluted 1:1 by weight (1 part graphite to 1 part coal ash). The volatilization curves obtained are shown in Figures 1, 2 and 3. Relative intensity values were obtained by the two step emulsion calibration procedure (see appendix). Note that only the curves for NBS coal and coal #3 are included, since the two samples are used in the semi-quant. and full quantitative analysis. The curves have also been grouped according to the relative intensity of the elements. Manganese and zinc are shown in Figure 1. Note that the base matrix of Ge is that of the synthetic standard, which is similar to coal sample #3.

From the time study curves it is evident that the volatilization of manganese is similar for the NBS coal ash and coal #3 ash. This also holds for zinc (see Figure 1). The relative intensities are however higher in the NBS coal matrix. On the same figure note how germanium burns off very quickly. Chromium and lead (Figure 2) volatilize very much like germanium. Vanadium and nickel in NBS coal ash volatilize differently from vanadium and nickel in coal #3 ash. Although the vanadium and nickel curves for coal #3 seem to be constant after 70 secs. at a very low relative intensity, they are nevertheless similar to the germanium

volatilization curve (see Figure 3). The reason for pointing out these similarities will be discussed in the next chapter.

TABLE VIII

Arcing Conditions for Time Study

Sample	Filter %	Current (amps)	Exposure (secs)	Anal. Gap (mm)	Slit Width
Fe (Iron)	100	4	15	4	20
NBS	100	11	10×10	4	20
fly ash	100	11	10×10	4	20
Coal #3	100	11	10×10	4	20

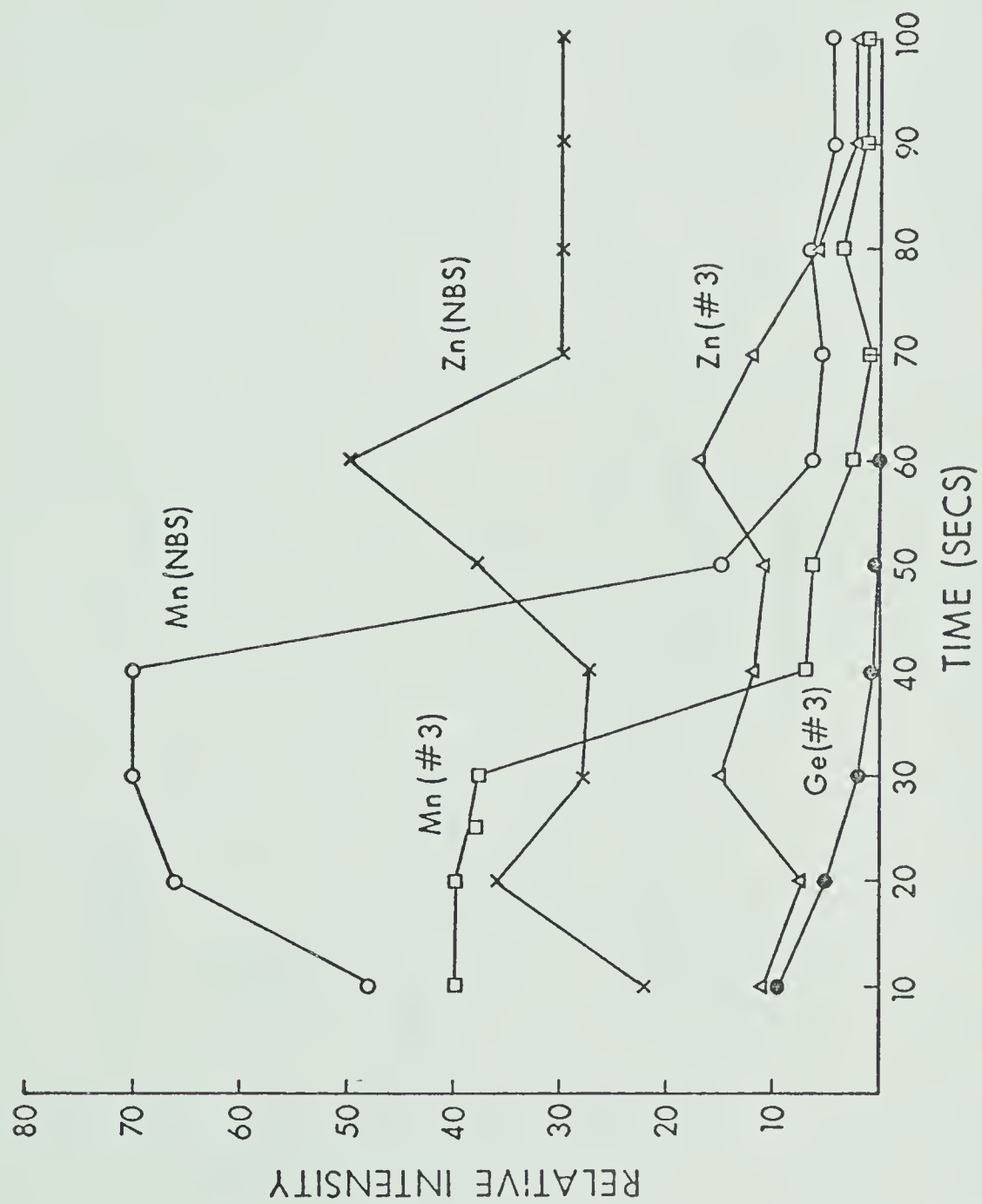


Figure 1. Time study plots for Mn and Zn in NBS coal and coal sample #3; and Ge in a synthetic standard matrix.

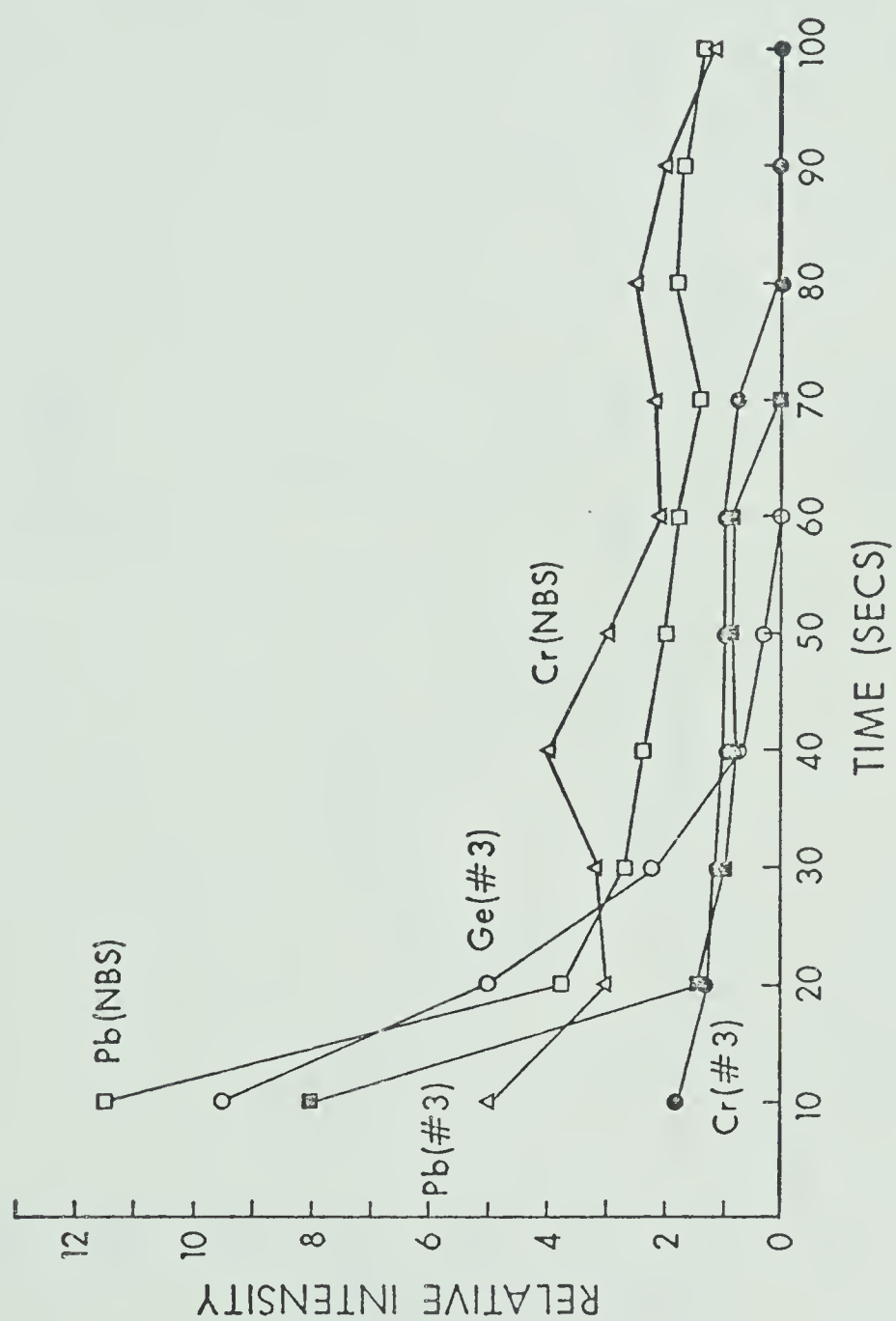


Figure 2. Time study plots for Pb and Cr in NBS coal and coal sample #3; and Ge in a synthetic standard matrix.

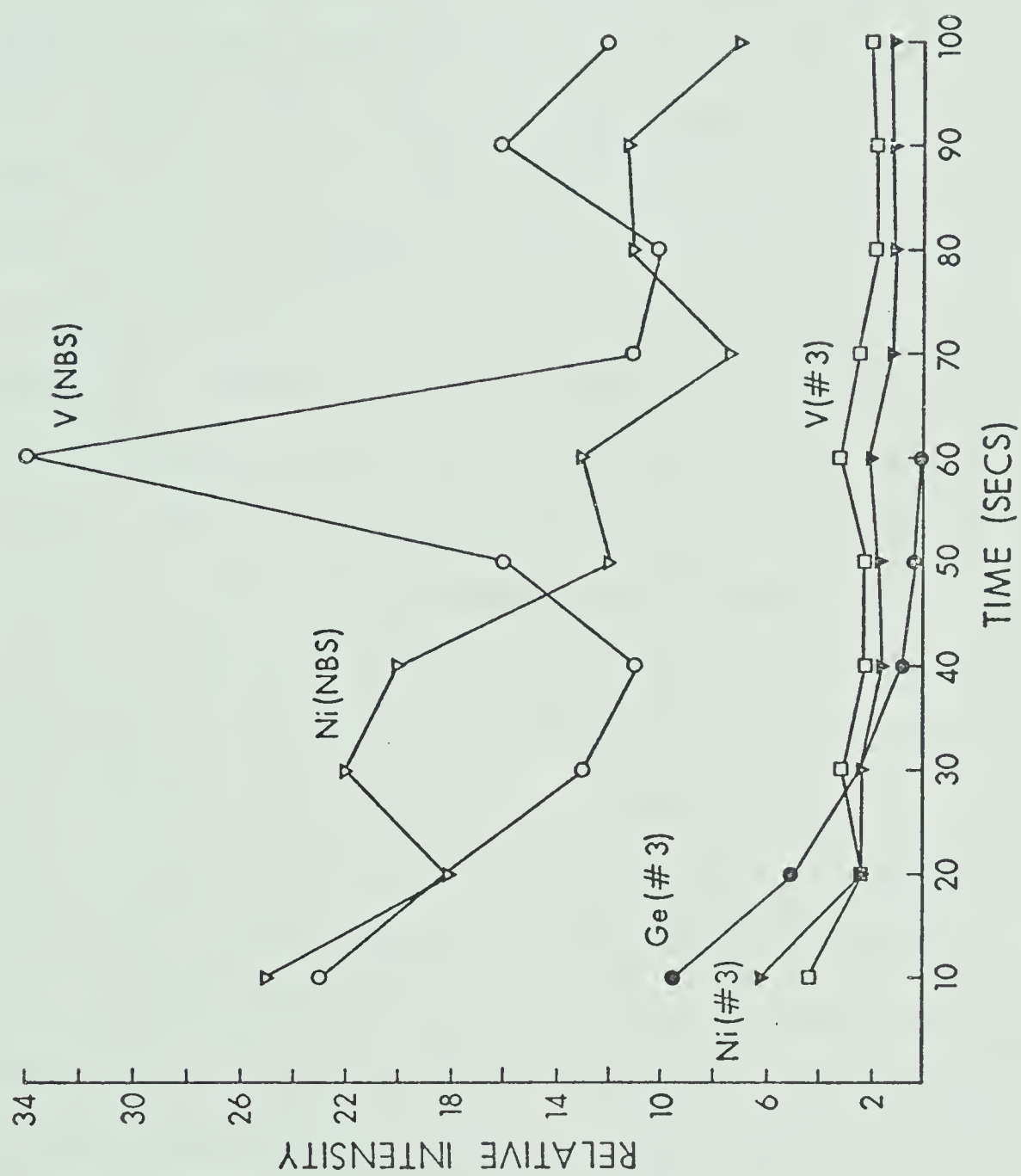


Figure 3. Time study plots for Ni and V in NBS coal and coal sample #3; and Ge in a synthetic standard matrix.

CHAPTER IV

Quantitative Analysis

A. SEMIQUANTITATIVE ANALYSIS

For many purposes, adequate accuracy can be obtained by making a visual comparison of the spectral intensities of the unknowns with those of standards. In most cases this kind of analysis is very valuable for preliminary surveys, which in many instances would delineate a problem, and aid in the selection of samples for more precise quantitative analysis. Harvey (32) developed a semiquantitative method for analyzing a wide variety of materials. Ahrens and Taylor (29) discuss various methods of semiquantitative analysis. What percentages or confidence levels are we actually dealing with when we carry out a semiquantitative procedure? According to the ASTM (33) definition of semiquantitative procedures, "... those procedures which measure the concentration of an element within a confidence level of 2/3 to 1-1/2 times the actual amount present."

Spex Spectrochemical G Standards were the standards used (catalogue no. 1002). In brief the G Standards consist of four concentration ranges, 0.1%, 0.01%, 0.001% to 0.0001% of 49 elements in graphite. No further dilution of the G Standards was done with graphite, they were all packed straight into the electrodes. Since our main objective was to develop a method for analyzing coal, three samples were used; the National Bureau of Standards reference material

1632 (NBS coal), NBS fly ash and one of the eighteen coal samples, #3. The NBS standard reference materials were used in the calibration of apparatus and methods used in the analyses. The certificate of analysis for the NBS reference material lists certified values based on the results of 4 to 17 determinations by each of at least two analytical techniques. The nine analytical techniques used did not include dc arc-optical emission spectrometry.

The arcing conditions are listed in Table IX. These parameters were arrived at after considerable study of different arcing conditions. Note that the G standards and samples were arced twice. First the samples were diluted 1:1 by weight with graphite and the neutral density filter on the dual illuminator was set at 6%. With this setting very intense lines were identified and compared more easily. The second set of arcing conditions for the samples was a 10:1 dilution by weight with graphite, and the neutral density filter set at 25%. Direct visual comparison was done with the samples and the G standards. The elements reported are those listed as certified in the National Bureau of Standards Certificate of Analysis. The semiquantitative results are shown in Table X. Note that because the standards differ by factors of 10 (i.e., 0.1, 0.01, 0.001, 0.0001), sample dilutions are not properly bracketed when visual estimates are made, also it is easy for such standards to be outside the latitude of the photographic emulsion, in fact, one can state that only two steps of the standards can be

TABLE IX

Arcing Conditions for Semiquantitative Analysis

<u>Sample</u>	<u>Filter %</u>	<u>Current (amps)</u>	<u>Exposure (secs)</u>	<u>Anal. Gap (mm)</u>	<u>Slit Width</u>
Fe	100	4	75	4	10
G1	6	11	90	4	10
G3	6	11	90	4	10
G4	6	11	90	4	10
fly (1:1)	6	11	90	4	10
NBS (1:1)	6	11	90	4	10
Coal #3 (1:1)	6	11	90	4	10
Fe	100	4	15	4	10
G1	25	11	90	4	10
G2	25	11	90	4	10
G3	25	11	90	4	10
G4	25	11	90	4	10
fly (10:1)	25	11	90	4	10
NBS (10:1)	25	11	90	4	10
Coal #3 (10:1)	25	11	90	4	10

TABLE X

Semiquantitative Analysis (ppm)

Element	NBS COAL		FLY ASH		Coal #3
	This Work	Certified Value	This Work	Certified Value	
Fe	1400→14000	8700	1400→14000	-	1400→14000
Mn	~140	40	~500	493	500
Zn	1400→14000	37	1000→10000	210	140→1400
V	1.4→14	35	100→1000	214	1.4→14
Pb	14→140	30	~100	70	14 →140
Cr	~14	20.2	100-300	139	~14
Cu	~14	18	~100	129	~14
Ni	1.4→14		~100	98	1.4→14

properly resolved by the emulsion. This was realised because the third step standard 0.001% showed very faint lines while the fourth standard was almost completely undetected. Furthermore, non-linearity of the emulsion above 85%T and below 5%T can be a problem, since the upper and lower concentration steps of the 4-part standards approach both these limiting values and the resulting analysis suffers accordingly. Remember however that dc arc semi-quantitative procedures are basically designed only to provide an order of magnitude result.

Bearing the above discussions in mind, the results obtained as shown in Table X can be understood and appreciated. Considering the individual elements, it is clear that the range of concentrations reported is quite large, for example Fe being estimated as 400 - 14000 ppm as compared to the certified value of 8,700 ppm for NBS coal. Elements that had lines that appeared to be close to one standard concentration were reported as having that concentration, Mn and Cr for example. The reported value for Zn is high both for NBS coal and fly ash. Note however, how the estimated values for fly ash closely resemble the certified values as compared to the NBS coal values. A reasonable explanation for this observation is that it can be attributed to the fact that very little sample preparation was necessary for the fly ash, since the elements were already in the metallic oxide state, whereas NBS coal had to be crushed, ashed, and ground to a fine powder before it was ready for analysis. This is an

important consideration since for samples already in the metallic oxide state like fly ash from coal plants, simultaneous multielement analysis and semiquantitative estimates can be done to a high level of confidence with dc arc-optical emission spectroscopy.

From the above considerations one can conclude that with standards which differ by less than factors of 10, that is 0.1, 0.03, 0.01, 0.003, etc., the accuracy of semiquantitative analysis will improve, because such standards will more easily bracket sample dilutions when visual estimates are made. Standards with the concentration range shown above would have most likely improved the results but at the time of the analysis they were not available.

B. MATRIX EFFECTS AND STANDARDS

Before a full quantitative method is developed for dc arc spectrochemical analysis fairly detailed information should be known about the chemical composition as well as the structure and the physical state of the sample, since those factors have a powerful influence on the excitation conditions and affect in one way or another the intensities of the relevant spectral lines. These internal influences have given rise to the term "matrix effects", which tends to suggest that it is mainly the matrix, i.e. the nature of the base and more generally that of its major constituents, that influences the excitation condition. Boumans (30) has divided the aggregate of matrix effects into two broad

categories, viz. the effects associated with the mechanism of entry of the material into the discharge gap and those pertaining to the processes that take place in the plasma.

Because a full quantitative method is to be developed the occurrence of matrix effects evokes the serious problem of accurate standardization. Note that spectrochemical determinations are usually based on the comparison of spectral-line intensities in the spectra of samples and in the spectra of standards; hence, it is essential that the elements sought are excited under entirely identical conditions in both samples and the standards. Ideal standards should have properties similar to those of the samples, the only difference being the concentration of the element to be determined.

To achieve these similarities between standards and samples, the major components of the base matrix of coal sample 3 were determined by atomic absorption analysis (34). The coal ash was decomposed in an acid digestion bomb as described by Bernas (21). Instrumental settings and analytical conditions for atomic absorption measurements are listed in Table XI, and the quantitative results for the major constituents are shown in Table XII. The percentages of elements reported are the amount in the coal ash, which are concentrated by a factor of almost 10 from that in the raw coal. From the table, silicon is the major component of the ash followed by aluminum, calcium, iron, titanium and magnesium.

TABLE XI

Operating Parameters for Atomic Absorption Analysis
of Coal Samples for Major Constituents

<u>Element</u>	<u>Lamp Current (MA)</u>	<u>Wavelength (nm)</u>	<u>Flame</u>
Aluminium	10	309.3	$\text{N}_2\text{O} - \text{C}_2\text{H}_4$
Calcium	3	422.7	$\text{N}_2\text{O} - \text{C}_2\text{H}_4$
Iron	5	248.3	$\text{N}_2\text{O} - \text{C}_2\text{H}_4$
Magnesium	3	285.2	$\text{N}_2\text{O} - \text{C}_2\text{H}_4$
Silicon	15	251.6	$\text{N}_2\text{O} - \text{C}_2\text{H}_4$
Titanium	10	364.3	$\text{N}_2\text{O} - \text{C}_2\text{H}_4$

* Slit width 0.1 nm.

TABLE XII
Quantitative Results for Major Constituents
by Atomic Absorption

Element	% Ash (Analytical Curve)	% Ash (Standard Addition)
Aluminium	10.5	18.4
Calcium	7.82	6.43
Iron	2.35	2.53
Magnesium	0.59	0.77
Silicon	32.5	35.1
Titanium	0.81	0.51

Knowing what the base matrix of the sample is made of or what its major components are, the next step is to prepare standards with a base matrix that would in all respect resemble that of the sample. To achieve this, high purity materials were obtained from SPEX industries. The compounds obtained were aluminum oxide cat. no. 1212 with 6-9s purity, iron oxide cat. no. 1232 with 5-9s purity and silicon oxide cat. no. 1250 with 6-9s+ purity. Calcium oxide was not available; the only calcium compound available was the carbonate with water of hydration, and for dc arc analysis this would be undesirable. These high purity materials were then combined in the right proportions to form the base matrix. Care was taken in the calculations to assure that the correct percentage of the elements were used rather than the oxide, since the percentages reported in Table XII were obtained for the elements rather than the elemental oxide. The mixture was then homogenized by mixing in a plastic vial with the SPEX mixer mill.

C. INTERNAL STANDARDIZATION

Another important consideration that reduces matrix effects and to some extent improves the accuracy of spectrochemical analysis usually involves the application of the internal standard principle. The internal standard principle requires the use of a reference element that is completely foreign to the samples and the standards, and should mimic the sought for element's behavior from sampling to detection.

A constant amount of this reference element is added to the samples and standards, and the relative concentration (C) of the analysis element (X) and the internal standard (R) are assumed to be some function of spectral intensity ratio.

$I(X)/I(R)$. That is

$$C(X)/C(R) = f I(X)/I(R)$$

The major problem in using the internal standard principle is to choose an analytical line so that under the influence of all experimental variables, except concentration, the intensity ratio will remain the same or constant. This involves the consideration of several major and a few less important factors when selecting an internal standard. Six of the major factors and three of the less important factors are listed in Ahrens and Taylor (29). Germanium was selected as the internal standard to be used, the reason for selecting Ge will be discussed in line with the major factors that should be considered in selecting an internal standard.

1. If an internal standard is to be added, as was done in this case, its concentration in the unknown sample should be negligibly low.
2. The rates at which internal standard and analysis element volatilize should be very similar; to assure this similarity a time study was done for the analysis elements and the internal standard. A brief description was presented in Chapter III as to the similarities of the curves of the analysis elements and the internal

standard. Most of the volatilization curves of the analysis elements resembled that of the internal standard, or in most cases the trend of the curves were similar especially for elements in coal sample #3. The elements that showed entirely different volatilization curves are Zn in NBS coal, nickel in NBS coal and to some extent vanadium in NBS coal.

3. Internal standard and analysis lines should have similar excitation potentials. The analysis lines for the elements determined are listed in Table XIII with the corresponding excitation potentials. Note that for the analysis lines of the elements for which excitation potentials were available, the excitation potential of the internal standard lines match relatively well that of the analysis element.
4. The internal standard line should be free from self-absorption. All three analysis lines of Ge which were used are free from self-absorption.
5. Analysis and internal standard lines should be roughly the same wavelength, so as to reduce errors that might occur in photographic measurement of radiant energy. The three analysis lines shown in Table XIII account for this.
6. The internal standard should be in a very high state of purity with respect to the elements sought. This is one advantage for using Ge since it can be obtained in a high state of purity.

TABLE XIII
Excitation Potential and Ionization Energies
of Elements to be Analysed Including
the Internal Standard

Element	Line (nm)	Excitation Potential (ev)	Ionization Potential
Cr	284.4	-	6.74
Mn	257.6	4.8	7.43
Ni	305.1	-	7.63
Pb	283.3	4.4	7.42
V	318.5	3.9	6.71
Zn	328.2	-	9.39
	334.5	7.75	-
Ge	265.1	4.8	8.13
	303.9	4.9	
	326.9	4.6	

Excitation potential values and ionization potential values are obtained from Ahrens and Taylor (29).

The above six major factors are the most important and one can conveniently state that the selected internal standard satisfies almost all the desired factors to a reasonable extent. Also from the qualitative results Ge is only present in one of the coal samples, hence its choice as an internal standard is quite suitable for the remaining samples; another plus for Ge is the fact that it has a very simple spectrum so that its interference with useful analytical lines is negligible.

D. PREPARING STANDARDS

To the prepared base matrix 0.1% Ge was added by weight. SPEX mix lot #573 which contains 1.25% of 49 elements was used as the source of elements for the standards. Appropriate amounts of the mix were added to the base matrix to obtain the following standards; 0.1%, 0.3%, 0.01%, 0.003% and 0.001% of the 49 elements in the mix (see Table XIV). With this concentration range in the standards, sample dilutions are more easily bracketed, the concentrations remain within the latitude of the spectroscopic emulsion which allows for a plot of the analytical curve with at least three standard concentrations. Note that the analytical curves are usually drawn as log-log plots, thus the concentrations of standards are quite suitable for such plots, since they provide evenly spaced points on a log-log axis.

At this point it should be pointed out that the SPEX mix used in the preparation of the standards also contains

TABLE XIV

Synthetic Standard in Base Matrix

Standard No.	SPEX Mix mg.	BASE* gms	Conc. %
1	104.2	1.2196	0.1
2	121.7 (Std. 1)	0.2839	0.03
3	68.4 (Std. 1)	0.6160	0.01
4	69.4 (Std. 1)	2.2439	0.003
5	81.4 (Std. 3)	0.7326	0.001

* The base was prepared as follows: 0.0144 gms. GeO_2 , 0.3360 gms. Fe_2O_3 , 1.9841 gms. Al_2O_3 and 6.9519 gms. SiO_2 .

Ge, so that instead of having 0.1% Ge in each of the standards the actual concentration of Ge in the standards was 0.2%, 0.13%, 0.11%, 0.103% and 0.101%. Those variable concentrations of the internal standard were taken into account when calculations of intensity ratios were made so as to normalize the amount of Ge present to 0.1% in all five standards.

Since NBS coal ash and coal #3 contain no Ge, the above correction was unnecessary, because the concentration of the internal standard was 0.1%.

E. ARCING CONDITIONS

The samples and standards were diluted 1:1 by weight with graphite and packed into electrodes similar to the ones described under qualitative analysis. The arcing conditions are listed in Table XV. Light entering the spectrograph from the dual illuminator was directed through a two-step filter which has one half transmitting 100% of the light while the other half transmits 33.11% of the light. This two-step filter is simply a quartz lens that is aluminized on one half and clear on the other. An exposure made through this filter produces spectral lines with one half being lighter than the other half. This provides an intensity ratio between the two halves determined by the percent transmittance of each half.

F. EMULSION CALIBRATION

As pointed out earlier the blackening on the developed

TABLE XV

Arcing Conditions for Quantitative Analysis

Sample	Filt. %	Curr. amps	Exposure (secs)	Anal. Gap (nm)	Slit Width	Slit Height mm
Fe	100	6	15	4	20	4
Std. 1	25	11	90	4	20	4
Std. 2	25	11	90	4	20	4
Std. 3	25	11	90	4	20	4
Std. 4	25	11	90	4	20	4
Std. 5	25	11	90	4	20	4
NBS Coal	25	11	90	4	20	4
Coal #3	25	11	90	4	20	4

emulsion is not directly related to the intensity of the light striking the emulsion in the spectrograph but is also dependent on the developing process, and the inherent characteristics of the emulsion itself. Generally a plot of film darkening, i.e. density of transmission of the film vs. log exposure, where exposure is defined as the product of density and time, should supply the necessary information. But for spectrochemistry, the information supplied by this curve is unsatisfactory because it is desirable to have a relationship between the emulsion darkening and a less unwieldy quantity than exposure as well as a quantity that is based upon a relative measurement rather than an absolute one. It is this requirement that has resulted in the construction of an emulsion calibration curve. This curve is often called the characteristic emulsion curve. It is a plot of a function of the relative transmission of the emulsion vs. a function of the exposure. It defines a relationship between the intensity of light reaching the emulsion and the resultant photochemical response of the emulsion. (The latter is dependent on the wavelength, thus energy, of the light striking the emulsion.)

The reason for using the two-step filter described above is to calibrate the emulsion on the photographic plates. Unlike films which usually have uniform emulsion thickness because they are coated by a continuous mechanical process, plates are usually coated by hand-pouring which in most cases results in non-uniform emulsion thickness.

Emulsion speed varies with grain size and the response of the emulsion to emitted radiation depends on the spectral region of interest. For example, in the visible region electromagnetic radiation penetrates a considerable distance into the emulsion. The thickness of the emulsion usually determines whether a given photon will activate a grain of the photosensitive material (AgBr), in its passage through the sensitive region. In the ultraviolet region photons are absorbed so quickly by the emulsion, that a given photon has an almost hundred percent chance of being absorbed within a short distance of the emulsion surface.

Hence, it seems obvious to conclude that non-uniformity of emulsion thickness is less important in the ultraviolet region (the most frequently used in spectrochemical analysis with photographic detectors); but photographic plates most widely used for spectrochemical analysis have a thin emulsion, therefore the non-uniform distribution of emulsion in the plate (Sa #1) even when used in the ultraviolet region does warrant some concern, especially when the photochemical reaction between photons and the photosensitive compounds in the emulsion producing a darkening on the emulsion after development is to be related to the amount of emitted radiation. This discrepancy resulting from non-uniform emulsion thickness is alleviated by calibrating the emulsion, when quantitative analysis is done.

A variety of methods have been proposed and used for emulsion calibration, including

1. Step Sector Method
2. Two line Method
3. Line Group Method
4. Two Step Filter Method.

In this analysis the two step filter method is used. An extensive discussion on the preliminary considerations for an emulsion calibration is detailed in Harveys' text (32). A detailed description of how the two-step filter method is manually used can be found in reference 33.

One of the common objections to the two-step filter method is the fact that two calibration curves have to be drawn, the preliminary curve and the emulsion calibration curve. Because manual methods are slow and liable to errors, computers and programmable calculators have been extensively employed in spectrographic calculations for the calibration of emulsions (35-39). Holcombe et al. (40) describes a FORTRAN-based photographic emulsion calibration procedure, which uses the two-step method and incorporates two new features, one limitation of this procedure is the fact that a dedicated computer is required. A general mathematical approach to emulsion calibration has also been proposed (36). Blevins and O'Neil (41) used the two-step filter method but an A-transform instead of the usual Seidel or Kaiser transform. A Fortran computer program computes the transform constant and obtains a linear equation for the emulsion calibration curve which is then used to program a desk calculator to convert transmittance readings to intensity ratio corrected

for background. Because of the limitations of time sharing computer facilities and in some cases the requirement of a dedicated computer, Bernard (42) developed a procedure that uses a desk programmable computer for calculating the calibration curve of a photographic emulsion, except that he used the step sector method. To calibrate the emulsion used in this analysis a procedure was developed, analogous to the manual methods described in the ASTM manual (33), using a T159 programmable pocket calculator. This program is different from those described earlier in that no computer assistance is required in obtaining the preliminary curve using the Seidel transform. A detailed description of the program is documented in the appendix.

G. RESULTS AND DISCUSSION

With the program developed above data were obtained for emulsion calibration curves for every 20.0 nm starting from 240.0 nm. An iron spectrum was used for all the calibrations. Extended log scale plots were drawn on 3 × 3 log paper for each of the regions calibrated. An example of the final emulsion calibration plot is shown in Fig. 4. From similar calibration curves, relative intensity readings were obtained for transmission data of analytical lines, internal standard lines and background. Background correction and corrections on the intensity of the internal standard, because of the variable concentrations were carried out. Working curves were drawn on log-log axes with the ratio of the intensity of

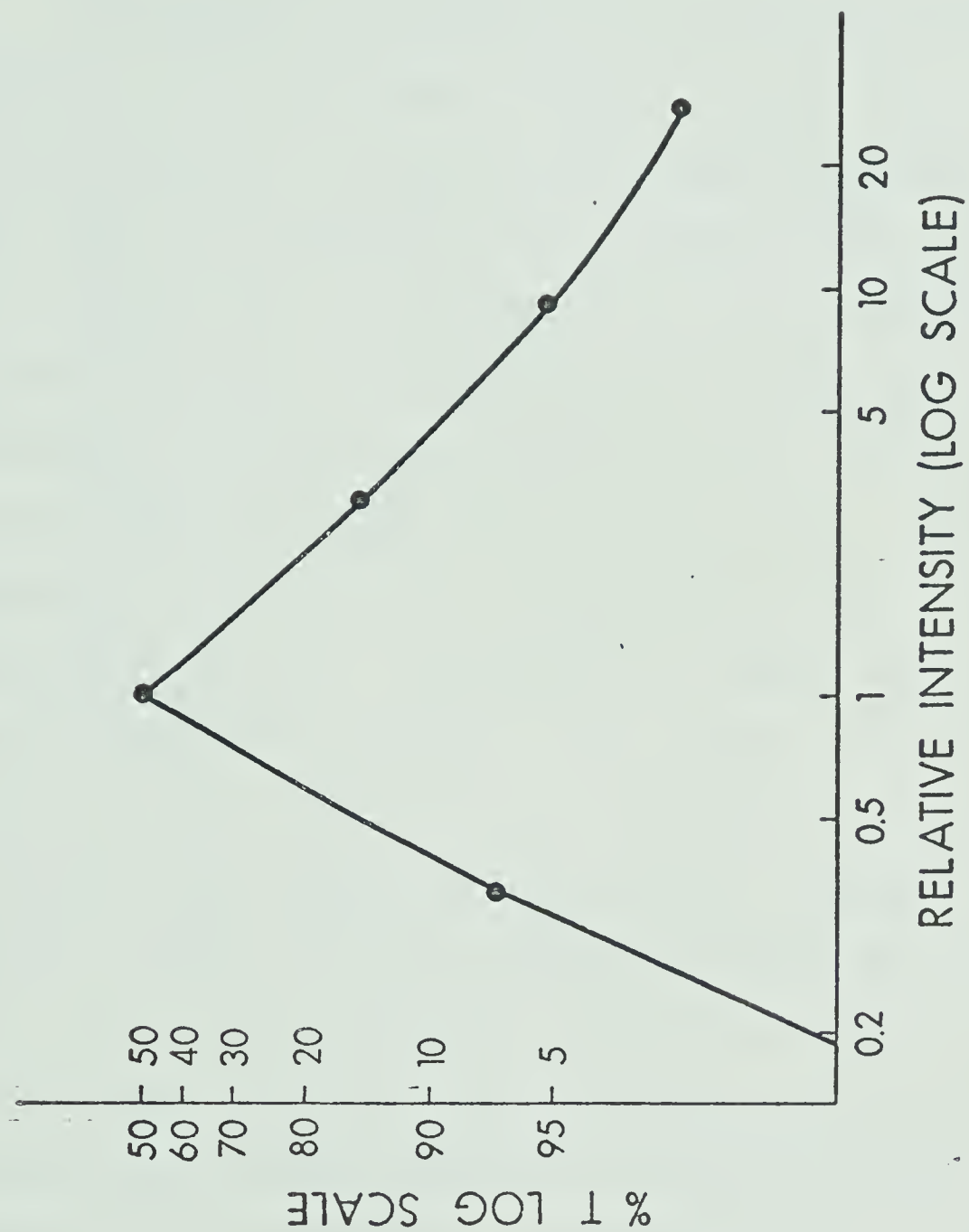


Figure 4. Final emulsion calibration plot.

the analysis line to the internal standard on the ordinate and the concentration of the analysis element expressed as percent element on the abscissa. The analytical curves are shown in Figures 5, 6 and 7.

An important consideration for analytical curves plotted on a logarithmic coordinate is the fact that the slope of the line should be 45°. When this condition is achieved the curve is considered to be a normal curve. This realization of a normal curve is difficult to achieve in dc arc spectrographic analysis. In the interest of obtaining the highest accuracy and simplifying standardization calculations, a unity slope analytical curve is desirable. Hence, it is important to realise and if possible improve off-slopes in analytical curves. The results of linear regression analysis on the analytical curves of the elements determined are shown in Table XVI. Almost all the analytical curves of the elements have slopes less than unity. Causes of non-unity slopes include using two points to define the analytical curve, the necessity of background correction, metallurgical differences resulting from increased percentage of a variable constituent directly under the internal standard line, and finally, self absorption. Analytical curves drawn on log-log coordinates do not usually show the characteristic bend of the analytical curve towards the concentration axis (abscissa) when self absorption is present but rather are straight with a slope of less than unity. Realizing that the physical and chemical nature of the dc arc discharge makes it prone to

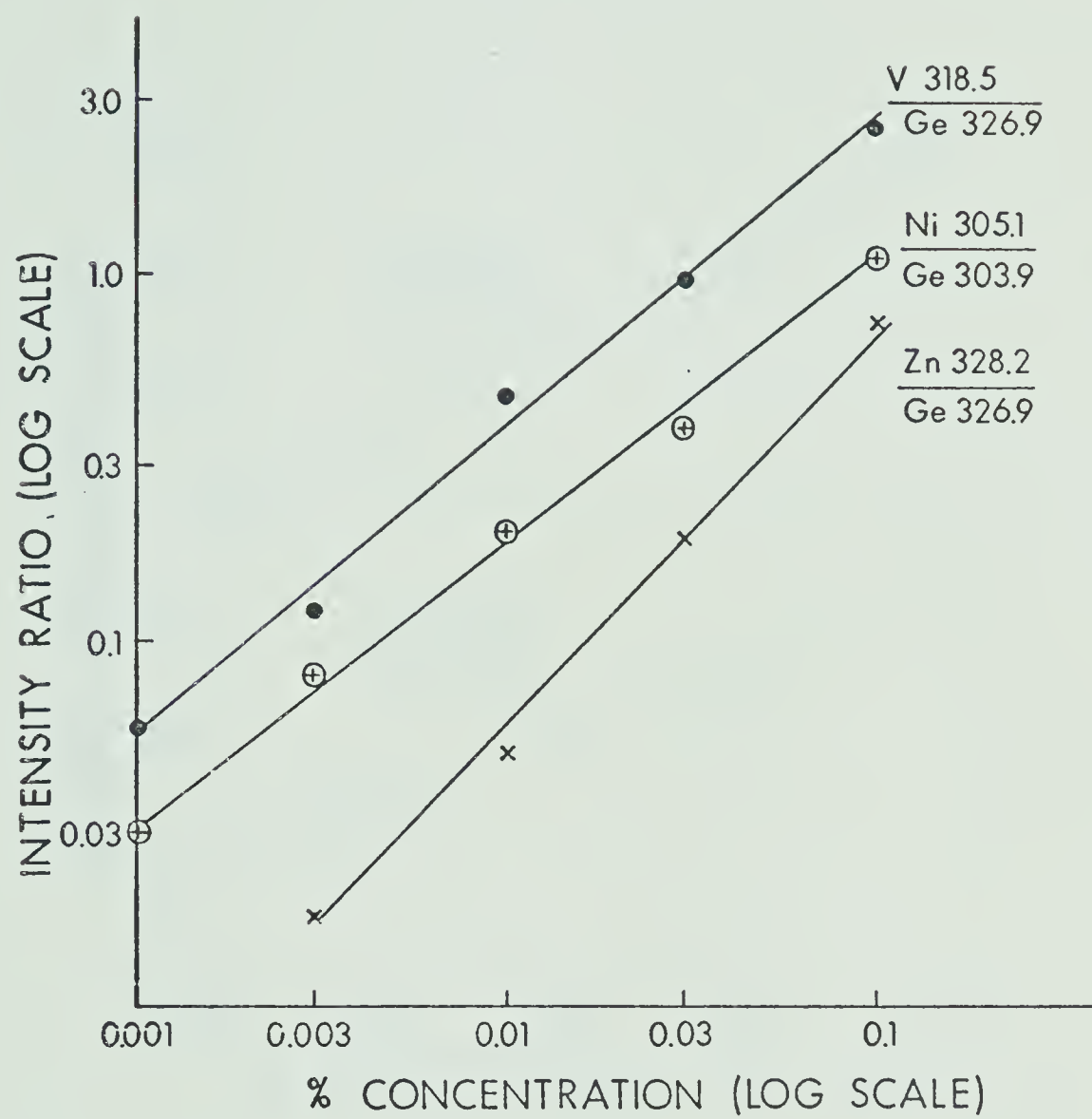


Figure 5. Analytical curves for V, Ni, and Zn.

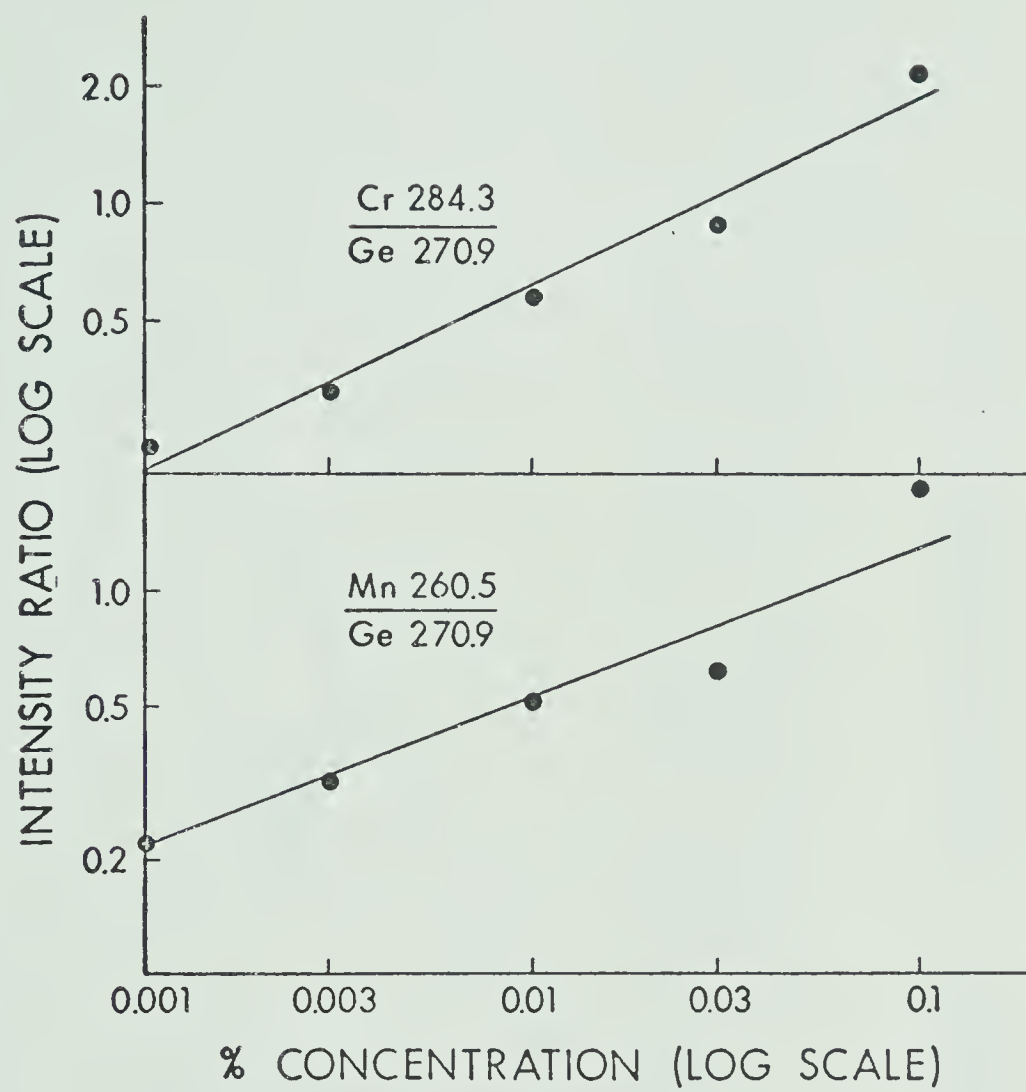


Figure 6. Analytical Curves for Cr, and Mn.

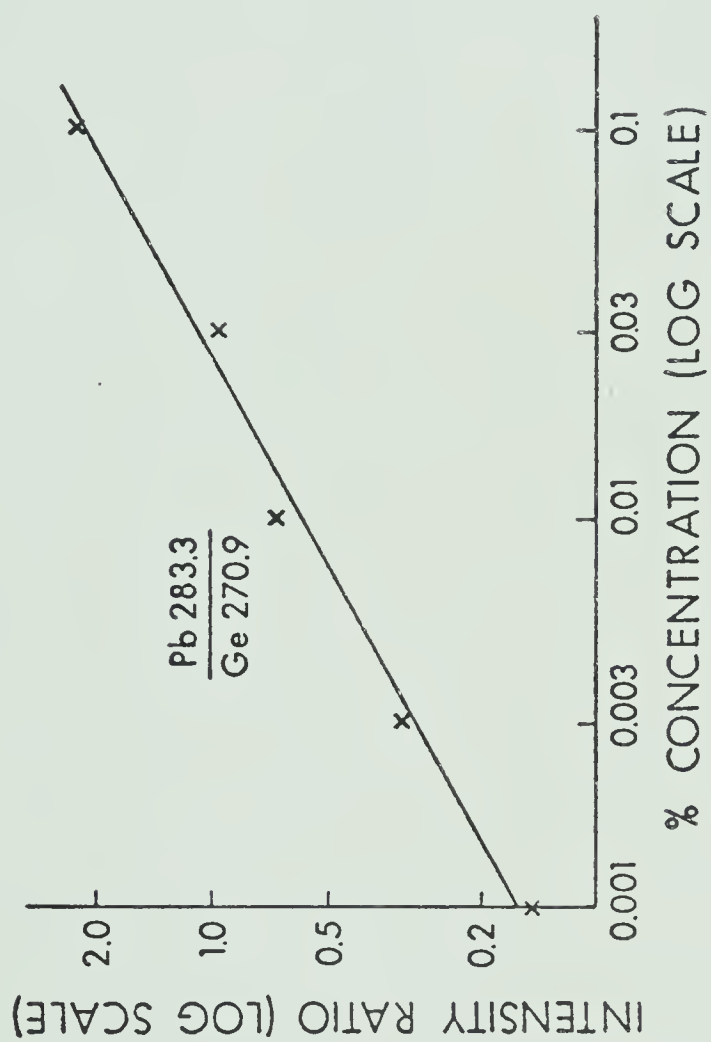


Figure 7. Analytical Curve for Pb.

TABLE XVI

Linear Regression Analysis of Analytical Curves

Element	Slope	Corr. Coeff.
Manganese	0.43	0.9685
Lead	0.57	0.9951
Chromium	0.48	0.9860
Nickel	0.76	0.9979
Zinc	1.05	0.9954
Vanadium	0.83	0.9962

self absorption, this effect is a common cause of off-slope analytical curves. In the construction of the analytical curves shown in Figures 5, 6 and 7, more than three points were used to define the curves, background correction was done for each line when necessary, and extreme care was taken to choose analytical lines for sought for elements and internal standard that were free from interferences. These lines were carefully chosen and checked from Zaidel (44). The off-slope of the working curves are all not of the same degree of shift from normal (see Mn and V), thus the possibility for the cause of the off-slope being the calibration of the emulsion is unlikely. From the above considerations the possible causes could be metallurgical differences due to increased percentage of a variable constituent, and/or the presence of ground state atoms or very low energy state atoms in the cooler outer fringe of the central hot core of the arc during arcing of samples resulting in self absorption.

From the working curves obtained, the percentage of elements in NBS coal and coal #3 were obtained, and the results calculated as ppm in whole coal are presented as ppm in whole coal. The results obtained (Table XVII) for Cr, Mn, Ni and V can be termed as reasonable when one considers the fact that the base matrix of the standard was not prepared to match NBS coal matrix but coal sample #3. As pointed out earlier the analytical methods used to determine the concentration of the elements in NBS coal were quite different from that used in this analysis, hence differences in sample preparation should be considered

TABLE XVII

D.C. Arc Trace Element Quantitative Results
(ppm in whole coal)

<u>Element</u>	<u>Line</u>	<u>NBS (Exp)</u>	<u>NBS (Lit)</u>	<u>Coal #3</u>
Cr	284.3	32.8	20.2±0.5	7.7
Mn	260.5	36.9	40±3	116.0
Ni	305.1	20.9	15±1	6.0
Pb	283.3	88.7	30±9	17.6
V	318.5	44.3	35±3	26.7
Zn	328.2	210	37±4	165

when considering the results reported (see Ruch et. al. (13)). This point can not be overemphasized when Table XVIII is considered. Only three samples are tabulated for each element, note that considerable variation occurs with the different analytical methods used for analysis. From the data reported in Table XVIII and that obtained from this analysis, one tends to conclude that these variations are mainly due to the inherent nature of coal with regards to the distribution of trace elements. The unusually high result obtained for Pb and Zn in particular are usually associated with localized mineralization and sample inhomogeneity (13). In the case of Zn improper internal standard could also be responsible, as Zn volatilizes differently from Ge (see volatilization curves, Fig. 2). Another important consideration for the high results of zinc could be due to temperature changes in the arc plasma, since zinc has been used as a thermometric element by Boumans (30). NBS coal and coal #3 have some sodium which would to some extent tend to lower the excitation temperature of the arc discharge, whereas the standard prepared had no sodium or alkali metal in its matrix. One last consideration of the results in Table XVII is that considering the NBS coal as a general representative of coal around North America (true for coals from coal mining industry in the USA) the element concentration obtained for coal #3 resembles that reported for NBS coal. Note also that as pointed out earlier the base matrix of the standards used to prepare working

TABLE XVIII

Trace Element Values in Moisture Free Coal Using
Using Different Analysis Methods

Coal Sample No	Element (ppm)				
	V Whole Coal X-Rf	V HTA PE-DR	V LTA OE-P		
C-16030	40	33	11		
C-16264	32	24	12		
C-16139	32	34	72		
	Ni Whole Coal X-Rf	Ni LTA AA	Ni HTA AA	Ni HTA OE-DR	Ni HTA OE-P
C-16030	35	33	38	47	58
C-15384	18	16	15	16	19
C-16317	27	27	24	36	34
	Zn Whole Coal X-Rf	Zn LTA AA	Zn HTA AA	Zn HTA OE-P	
C-17001	68	184	171	117	
C-16139	44	86	-	140	
C-14721	123	294	221	85	
	Pb Whole Coal X-Rf	Pb LTA AA	Pb HTA AA	Pb HTA OE-DR	Pb HTA OE-P
C-15117	83	163	188	249	135
C-15944	106	197	-	99	258
C-51	51	86	57	64	53
	Cr LTA AA	Cr HTA AA	Cr HTA OE-DR	Cr HTA OE-P	
C-16030	21	29	17	35	
C-14970	18	17	12	19	
C-13464	-	-	33	74	

LTA = Low temperature ash.

HTA = High temperature ash.

X-Rf = X-ray fluorescence.

OE-DR = Optical emission - direct reading.

OE-P = Optical emission - photographic.

AA = Atomic absorption.

All data from Ruch et al. (13).

curves was based on the base matrix of coal #3.

H. PRECISION STUDY

One disadvantage of the dc arc optical emission technique when a photographic plate is used for analysis is the lack of precision. Percent relative standard deviations as high as 40 are not uncommon. This problem can be reduced by enclosing the arc discharge in a controlled atmosphere in order to stabilise it. One of the most common devices used to achieve this is the Stallwood jet (45).

A precision study on vanadium and manganese was carried out with and without the Stallwood jet. A SPEX enclosed Stallwood jet (cat. #9027) and a SPEX quartz DOME (cat #9026) were used when the precision study was carried out with the air Stallwood jet. All excitation conditions were the same as for the quantitative analysis described earlier. Ordinary air was used as the surrounding gas. When the jet was used the indicator for air flow in the Arc/Spark stand was set at 16 SCFH while the gas tank pressure was 30 psi. Triplicate arcings were done for the determination of vanadium and manganese with and without the air Stallwood jet. The results obtained are shown in Tables XIX and XX. The analytical curves for vanadium with and without an air Stallwood are shown in Fig. 8, while the analytical curves for manganese with and without an air Stallwood jet are shown in Fig. 9. The results for V with the air Stallwood jet show high relative standard deviations for three of the concentration ranges with only one concentration range having a percent relative standard

deviation of less than 4. The values for the manganese with the air Stallwood jet are much lower when compared to those of vanadium. Without the Stallwood jet the percent relative standard deviations are quite high in both cases (see Tables XX(a) and XX(b)). This boils down to the fact that the precision values shown in Tables XIX and XX indicate relatively poor precision for the method, but this is not atypical of quantitative dc arc emission spectroscopy. The precision values obtained in this analysis are comparable to or better than that obtained by many workers. Ruch et al. (13) for example, shows a percent relative standard deviation of 30 for vanadium with the same analytical line as was used in this analysis, and 79 for manganese. The percent relative standard deviation obtained for vanadium and manganese with the Stallwood air jet can be estimated as being 17 and 11, and without the air Stallwood jet, 20 and 25. Hence the precision obtained with the Stallwood air jet is much better than that reported by Ruch. Moreover, the results obtained show that the use of the air Stallwood jet does improve the precision of results when quantitative dc arc is the analysis method.

TABLE XIX(a)

Precision Study on Vanadium With Air Stallwood Jet

% Element	IV/IGe	IV/IGe	IV/IGe	Ave.	S.D.	%R.S.D.
0.1	2.83	1.92	2.78	2.51	0.51	20.4
0.03	0.69	0.73	0.68	0.70	0.02	3.8
0.01	0.28	0.22	0.31	0.27	0.05	17.0
0.003	0.10	0.15	0.09	0.11	0.03	28.4

TABLE XIX(b)

Precision Study on Manganese with Air Stallwood Jet

% Element	IMn/IGe	IMn/IGe	IMn/IGe	Ave.	%R.S.D.
0.1	2.1	2.2	2.7	2.3	13.8
0.03	0.8	0.9	0.83	0.84	6.1
0.01	0.39	0.33	0.30	0.34	13.5
0.003	0.23	0.28	0.24	0.25	10.6

TABLE XX(a)

Precision Study Data on Vanadium Without Air Stallwood Jet

% Element	IV/IGe	IV/IGe	IV/IGe	Ave.	S.D.	%R.S.D.
0.1	1.22	1.60	1.44	1.44	0.20	13.7
0.03	0.61	0.96	0.60	0.72	0.21	28.5
0.01	0.24	0.24	0.31	0.26	0.04	16.3
0.003	0.14	0.18	0.12	0.15	0.03	20.8

TABLE XX(b)

Precision Study on Manganese Without Air Stallwood Jet

% Element	IMn/Ige	IMn/IGe	IMn/IGe	Ave.	%R.S.D.
0.1	3.75	4.88	4.02	4.2	14
0.03	1.55	0.63	1.2	1.1	41
0.01	0.83	0.60	0.63	0.68	18
0.003	0.31	0.36	0.51	0.40	27

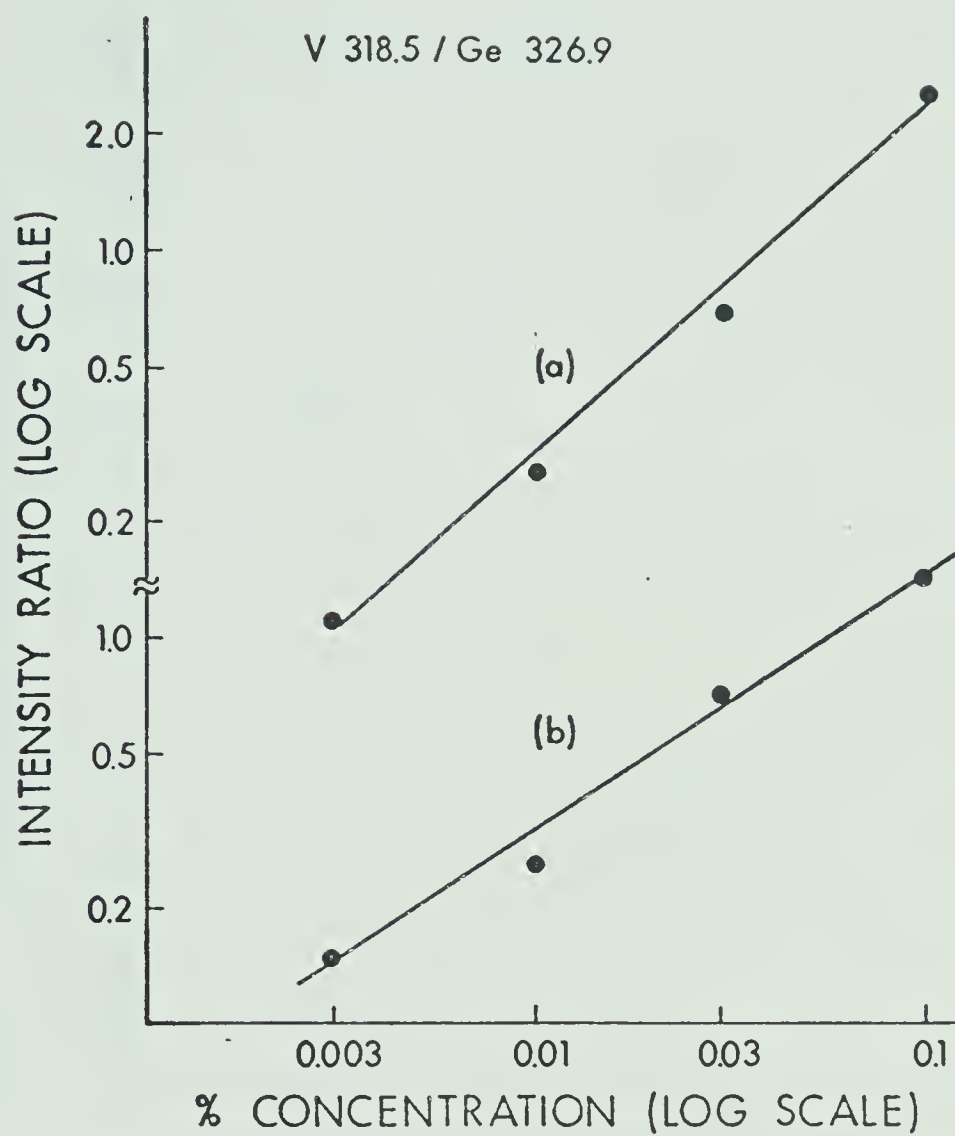


Figure 8. (a) Analytical curve for V with an Air Stallwood Jet.
(b) Analytical curve for V without an Air Stallwood Jet.

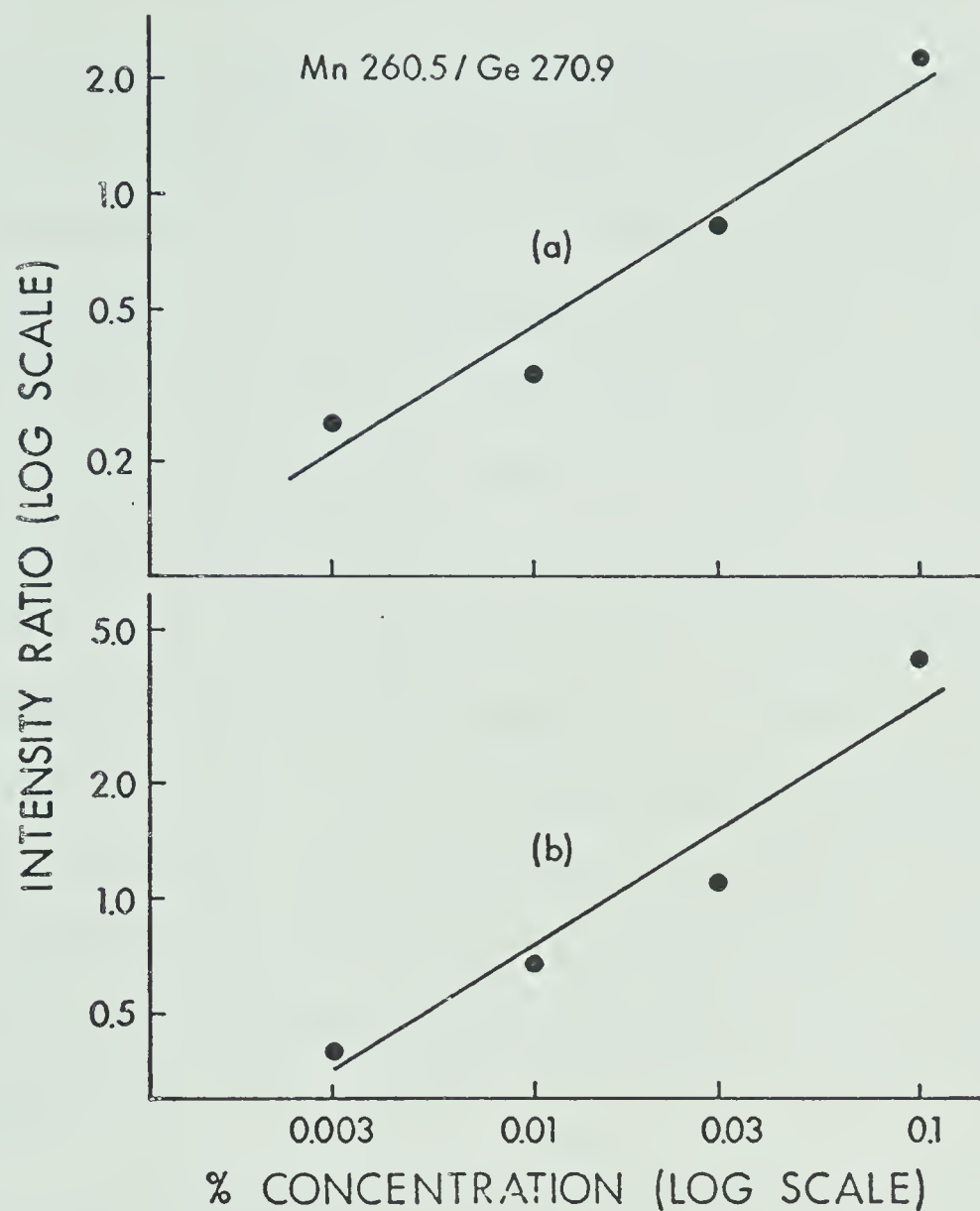


Figure 9. (a) Analytical curve for Mn with an Air Stallwood Jet.
(b) Analytical curve for Mn without an Air Stallwood Jet.

CHAPTER V

Inductively Coupled Plasma with a Photographic Detector

The use of inductively coupled plasmas as excitation sources for trace metal determination has been extensively investigated by many authors including Greenfield (46), Wendt and Fassel (47) and Scott et al. (48). Detection limits are in the range of 0.1 - 100 $\mu\text{g/ml}$ in the solution or 0.01 - 10 ppm ($=\mu\text{g/g}$) in the dissolved solid sample (1% M/V) for approximately 15 s-integration (49). With such detection limits, the use of an ICP in conjunction with a spectrograph could provide superior results to those obtained with the dc arc source-spectrograph combination. With this in mind a short preliminary study of the analytical applicability of the ICP source-spectrograph combination for the simultaneous trace element analysis of coal ash was undertaken.

A. PRELIMINARY SURVEY

As indicated above solid samples must be dissolved and put into solution for analysis with an inductively coupled plasma. The dissolution process described earlier when solid samples were dissolved for atomic absorption analysis was used, that is the fluoroboric acid digestion bomb method. Accurately weighed samples of NBS coal and coal #3 were dissolved by the above method and made up to 100 ml respectively. Before these solutions were analysed, standard solutions of Fe, V, Mn, Cr,

Pb, Ni, and Zn at concentrations of 0.1, 1.0, and 10.0 ppm (except Fe - 1000 ppm), were analysed with the ICP and spectrograph to establish among other things optimum operating conditions, and moreover to detect useful analytical lines on the photographic plate after development. This last consideration is very important because the ICP source is quite a different source from the dc arc in that it has a higher excitation temperature than the dc arc. What this eventually amounts to is that the ICP is a much hotter source than the dc arc, consequently there will be very few atom line emissions and most of the emission signals will come from ion lines, which to some extent would be similar to spark emission. The operating parameters of the ICP and spectrograph are shown in Table XXI, while the solutions analysed and the operating conditions are shown in Table XXII. The photographic plate was then developed and analytical lines identified with the aid of a standard plate and Zeidel's (44) wavelength tables.

Most of the spark lines on the standard plate were used in the identification of useful analytical lines of the elements analyzed. The useful analytical lines detected and the corresponding concentrations are shown in Tables XXIII to XXVII. Note that no lines were detected for Zn in the spectral region used, since most of the ion lines that are sensitive to be detected are outside the spectral region used; that is the 240.0 nm to 340.0 nm region on the higher resolution grating. Some examples include P 177.4 nm, As 189.0 nm

TABLE XXI

Operating Parameters of the ICP and Spectrograph

Coolant Plasma gas	17 LPM
Nebulizer Pressure	14 psi
Incident Power	2.0 kw
Reflected Power	25 watts
Loading	99
Tuning	171
Aux.	0
Aerosol	1.0 L/M
Spectrograph	dual grating - 240.0-340.0 nm - 240.0-440.0 nm
Slit width	10 μ
Slit height	1.5 mm

TABLE XXII

Solutions Analyzed with Exposure Times

Solution	Conc. (ppm)	Exposure Time (Secs)
Fe	1000	30
V	0.1	60
	1.0	60
	10.0	60
Mn	0.1	60
	1.0	60
	10.0	60
Cr	0.1	60
	1.0	60
	10.0	60
Pb	0.1	60
	1.0	60
	10.0	60
Ni	0.1	60
	1.0	60
	10.0	60
Zn	0.1	60
	1.0	60
	10.0	60
Cu	0.1	60
	1.0	60
	10.0	60
NBS Coal		60
Coal #3		60
Fe	1000	60

After each element, the nebulizer was flushed with HNO_3 and distilled water for 1 min.

TABLE XXIII

ICP - Photographic Analytical Lines for Mn

Conc. (ppm)	Line (nm)	Comment
0.1	-	-
1.0, 10	257.6	weak, strong
1.0, 10	259.3	weak, strong
1.0, 10	260.5	weak, strong
1.0, 10	279.4	very weak, strong
1.0, 10	279.8	very weak, strong
1.0, 10	280.1	very weak, strong
1.0, 10	+403.2	fairly strong, strong
1.0, 10	+403.4	fairly strong, strong
1.0, 10	+403.0	fairly strong, strong

+ With lower resolution grating.

TABLE XXIV

ICP - Photographic useful Analytical Lines for V

Conc. (ppm)	Line (nm)	Comments
0.1, 1.0	312.5	very weak, strong
1.0, 10.0	268.7	weak, strong
1.0, 10.0	309.3	weak, strong
1.0, 10.0	311.0	weak, strong
1.0, 10.0	311.8	weak, strong
1.0, 10.0	312.5	weak, strong
1.0, 10.0	318.5	very weak, strong
1.0, 10.0	*326.7	very weak, strong
1.0, 10.0	*327.1	very weak, strong
1.0, 10.0	*327.6	very weak, strong

* Lines that are not on standard plate, but reported in Zeidel's wavelength table.

TABLE XXV

ICP - Photographic Useful Analytical Lines for Cr

Conc. (ppm)	Line (nm)	Comments
0.1	-	not detected
1.0, 10	*267.7	very very faint, strong
10	*276.2	fairly strong, no
	*276.6	interference
1.0, 10	283.5	overlap with
	284.3	iron
10	*302.1	strong
	*301.7	strong
1.0, 10	+*357.8	weak, strong
	+*359.8	weak, strong
10	+*360.5	strong
1.0, 10	+425.4	weak, strong
	+427.4	weak, strong
	+428.9	weak, strong

* Lines that are not on standard plate but reported in Zeidel's wavelength table.

+ With lower resolution grating.

TABLE XXVI

ICP - Photographic Useful Analytical Lines for Pb

Conc. (ppm)	Line (nm)	Comments
0.1	-	not detected
1.0	-	not detected
10.0	283.3	*weak
10.0	+368.3	very weak
10.0	+405.7	weak

* This line can be used for analysis if operating parameters are further optimised.

+ With lower resolution grating.

TABLE XXVII

ICP - Photographic Useful Analytical Lines for Ni

Conc. (ppm)	Line (nm)	Comment
0.1	-	not detected
1.0, 10.0	300.2	very faint, strong
	305.0	very faint, very faint
10	300.3	strong
	301.2	strong
	303.7	strong
	+352.4	weak
	+351.5	weak
	+361.9	weak

None of the lines reported above are listed on the standard plate, but are reported in Zeidel's wavelength table.

+ With lower resolution grating.

TABLE XXVIII

ICP - Photographic Useful Analytical Lines for Cu

Conc. (ppm)	Line (nm)	Comment
0.1, 1.0, 10.0	324.7	faint, strong, very strong
1.0, 10	327.3	strong, very strong

and Zn 213.8 nm all of which have been reported to be extremely sensitive lines in the ICP. At the other wavelength extreme are Pb 405.7 nm, Cs 852.1 nm, and K 769.9 nm, the last two being in the far red region, which are the most sensitive and outside this range. In most of the elements analyzed the 0.1 ppm concentration was not detected or is reported as very weak. Because of the known detection limits of the ICP, it would seem that the latitude of the photographic emulsion does have a considerable effect on the detection limits of most elements. But again the operating parameters of the ICP can be optimized to improve on the detection limits. This was realised later after the nebuliser pressure was decreased from 14 psi to 10 psi. This reduction in pressure resulted in a more intense source, temperature wise, and thus creates the proper environment for ion line emission. Also since photographic emulsions exhibit wide variations in sensitivity at different wavelengths, specially treated emulsions can be obtained that are sensitive in regions where the present emulsion used is not. The spectral region that our present emulsion covers in terms of sensitivity is from around 240.0 nm to a little less than 450.0 nm.

Since this work is only a preliminary survey no extensive study was done to improve the detection limits. However, the slit width was changed from 10 μ to 20 μ and the exposure time was doubled to 120 secs. It is important to note that this effect of a long exposure could not be relied upon, since the failure

of the reciprocity law is a common spectrographic effect; that is in a photochemical reaction, a constant effect is produced if the product of time and radiant power is a constant, or rather the extent of a photochemical reaction is proportional to the total energy employed. The failure of this law results from the fact that photographic emulsions show a loss in sensitivity at very low or very high exposure levels. Also as pointed out earlier the nebuliser pressure was reduced to 10 psi. These changes did improve the detection limits especially of Mn and V. It was realised that the most important was the change in the nebuliser pressure. This indicates that the already excellent detection limits reported for the ICP with other detectors may well be achieved with the ICP and the photographic plate if careful optimization of the operating parameters of the ICP is carried out.

One distinguishing characteristic of the photographic spectrum obtained with the ICP is the absence of the cyanogen bands and heavy background due to electrode emission characteristic of the dc arc. However the spectrum was not entirely clean because two hydroxyl bands from water are very prevalent and predominate around 281.1 nm to 293.0 nm and 306.4 nm to the end of the spectrum ~340.0 nm. Generally the spectrum was clear, but in the regions where OH bands predominate detecting useful analytical lines can be difficult. Unlike CN bands in the dc arc, which can be eliminated by enclosing

the dc arc in a controlled atmosphere, the hydroxyl bands from the plasma cannot be eliminated since water is the main solvent used with the ICP. However, with a proper understanding and characterization of analytical information obtained from the ICP with a photographic plate, the problem of OH band emission can be managed.

B. PRECISION STUDY

Having arrived at reasonable operating conditions, a standard mixture containing V and Mn was prepared so as to bracket the concentration of V and Mn in NBS coal and coal #3. The following concentrations were prepared; 0.5, 1.0, 2.0, 5.0 and 10.0 ppm, in each sample a constant amount of Ge was added to act as an internal standard if desired. Triplicate runs of each concentration and sample were carried out. The operating conditions of the ICP and spectrograph are shown in Table XXIX.

Iron produced a rich spectrum that was suitable for emulsion calibration, but tailing of spectral lines in certain regions made calibration difficult with the two step filter method. This problem was more evident around the 310.0 nm region and prevented the use of very sensitive vanadium lines, since the emulsion around this region cannot be properly calibrated. The results obtained for Mn and V are listed in Tables XXX and XXXI. The analytical curves obtained for V and Mn are shown in Figures 10 and 11.

TABLE XXIX

Operating Conditions of the ICP and Spectrograph

Nebuliser Pressure	10 psi
Aerosol	1.0 LPM
Coolant Plasma Gas	17 LPM
Incident Power	2.0 kw
Reflected Power	25 watts
Loading	99
Tuning	77
Aux.	0
Spectral range	240.0 → 340.0 nm
Slit width	20μ
Slit Height	4 mm
Filter	2 Step - 33.11% - 100%
Exposure for Samples	100 secs

(ICP, plasma therm, commercial model 2500)

TABLE XXX

Precision Study on Manganese with an Inductively
Coupled Plasma and a Photographic Plate

Conc. (ppm)	I ₍₁₎	I ₍₂₎	I ₍₃₎	Ave.	S.D.	%R.S.D.
0.5	2.50	2.53	2.50	2.51	0.017	0.7
1.0	4.8	4.9	5.1	4.93	0.15	3.1
2.0	7.5	7.5	7.8	7.6	0.17	2.3
5.0	17.0	17.2	17.5	17.6	0.81	4.6
10.0	35.0	35.0	35.0	35.0	0	0
NBS Coal	5.36	5.24	-	5.3	0.08	1.6
Mn in NBS Coal = 45 ppm (lit. 40 \pm 3)						

TABLE XXXI

Precision Study on Vanadium with an Inductively
Coupled Plasma and a Photographic Plate

Conc. (ppm)	I ₍₁₎	I ₍₂₎	I ₍₃₎	Ave.	S.D.	%R.S.D.
0.5	0.54	0.55	0.56	0.55	0.01	1.8
1.0	0.86	0.90	0.87	0.88	0.02	2.4
2.0	1.23	1.25	1.25	1.24	0.01	0.93
5.0	2.4	2.4	2.4	2.40	--	0
10.0	4.2	4.1	4.1	4.10	0.006	1.4
NBS	0.55					

V in NBS Coal = 28 ppm (lit 35±3)

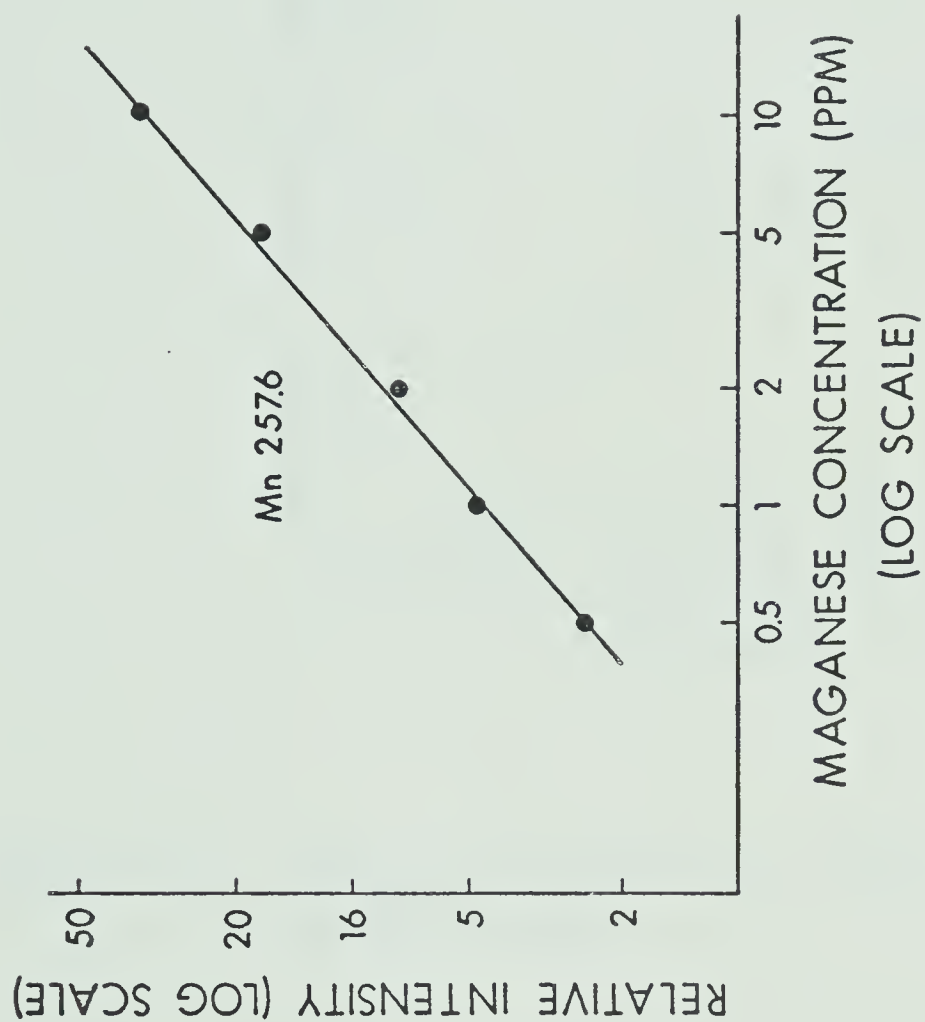


Figure 10. Analytical curve for Mn with an inductively coupled plasma.

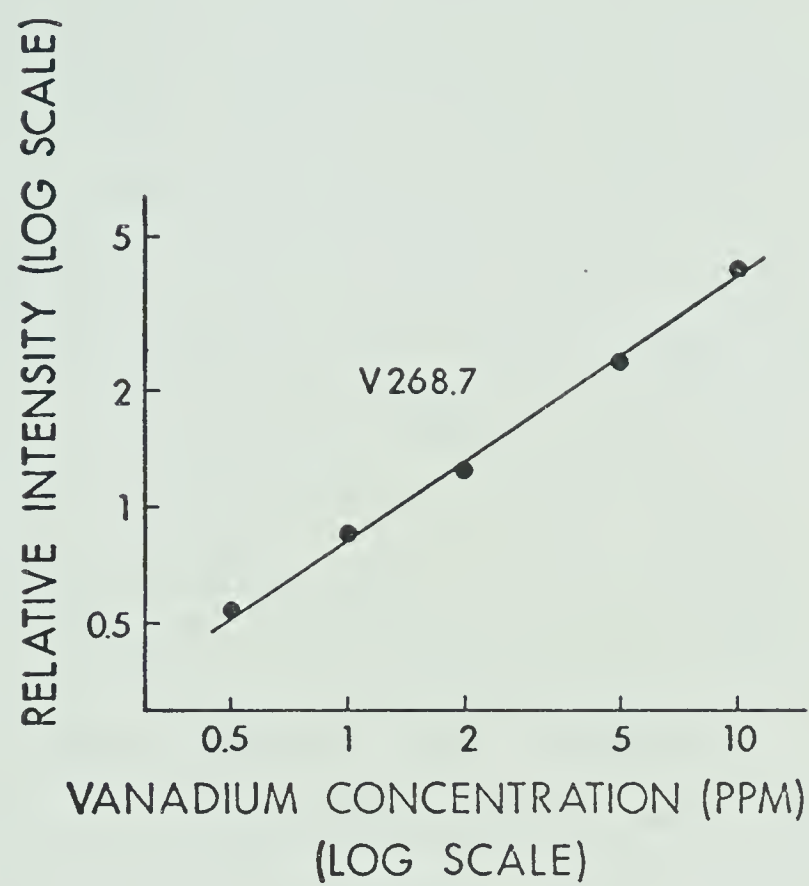


Figure 11. Analytical curve for V with an inductively coupled plasma.

C. DISCUSSION AND RESULTS

The analytical curves for Mn and V show great improvement over similar curves with the dc arc and a Stallwood jet. The intensity values for Mn and V were obtained with no internal standard and no background correction; however it should be pointed out that the analytical line used for vanadium is not one of the most sensitive, and interference effects could be responsible for the off-slope. The precision values are also greatly improved over those of the Stallwood jet dc arc result. The percent relative standard deviation for vanadium can be estimated as 1.6 and manganese 2.4. These results indicate that the ICP is a very stable source compared to the dc arc, and moreover the emulsion on the photographic plate responds quite uniformly. With the ICP the main source of fluctuations that could affect the precision is the nebuliser pressure. Hence considering all the possible sources of error in spectrochemical analysis lack of precision is to a considerable extent determined by the source or some characteristic of the source. This does not by any means eliminate the photographic emulsion as a contributing factor to the precision of the analysis.

CHAPTER VI

Conclusion

The methods developed so far give results that are comparable to other methods, the most important consideration is the fact that with the dc arc careful control is essential for accurate and precise results in semiquantitative and full quantitative analysis whereas in qualitative estimates the dc arc is a very powerful tool especially for solid samples. The results obtained with the inductively coupled plasma indicate that this source could well replace the dc arc as a universal source despite the fact that extensive sample preparation is required, especially when solids are to be analyzed, but the precision and accuracy of the results obtained are worth the effort. In fact stock standard solutions could be prepared that are similar to the solid standards Spex mix containing various concentrations of about 50 elements. These standards could then be used in semiquantitative and even full quantitative procedures for solution samples.

Very little on the use of the ICP and a photographic detector has been reported. However, this preliminary survey shows that for this combination to be extensively used, preliminary and investigative studies must be carried out, especially in the area of identifying useful analytical lines within the useful dynamic range of the photographic detector.

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APPENDIX

Complete photographic emulsion calibration with a pocket programmable T159 calculator.

The two step method is used in the development of the program. In brief, the two step filter is simply a circular piece of quartz glass that is aluminised on one half and clear on the other. When an exposure is made through this filter, spectral lines are produced with one half being lighter than the other half. This provides an intensity ratio between the two halves determined by the percent transmittance of each half.

A table of percent transmittance for the spectral region of interest is then recorded from a densitometer. These percent transmittance values are converted to siedel values, using the modified siedel function $\Delta = \log\left(\frac{100}{\%T} - 1\right)$. A preliminary curve is then constructed with Δ filtered step on the x axis or abscissa and Δ cleared step on the y axis or ordinate. Using the built in functions of the calculator the preliminary curve is constructed and the values of the final curve obtained by a procedure analogous to the manual methods described elsewhere (33). Since the choice of the starting value for percent transmittance having a relative intensity of 1 is arbitrary, the user has the choice of selecting the starting value. Also included in the program is the seven point method for obtaining the final curve. This involves using the coefficients of the preliminary curve to obtain seven points, the central value having a Δ value of 0 corresponding

to 50%T with a relative intensity of 1. Figure 12 shows a flow chart and description of the program.

To Use The Program.

1. Obtain transmission data from the photographic plate for spectral region of interest. Usually not more than twenty readings are taken between each 10 or 20 nm within the spectral region of interest. At least forty DATA MEMORY REGISTERS (DMR) must be allocated for storing transmission DATA. If DMR is represented as N, then $(13 < N < 56)$. On the transmission data sheet assign memory locations to transmittance values for easy entry into Calculator. Assign the highest DMR to the first filtered percent trans value and the lowest DMR to the last cleared percent trans value, example:

DMR	%T filtered step	DMR	%T cleared step
N	78.2	N-2	52.3
N-1	68.5	N-3	24.1

If N is 55 then the last value of percent T filtered step will be stored in DMR 54, the first value of percent T cleared step will be stored in DMR 53, and the last value of percent T cleared step will be stored in DMR 52.

2. Enter the transmission data in the appropriate storage locations and also the highest data register used the lowest data register used and the 1st DMR of %T cleared step; the entered transmission data is then converted to seidel values, the converted values are then displayed

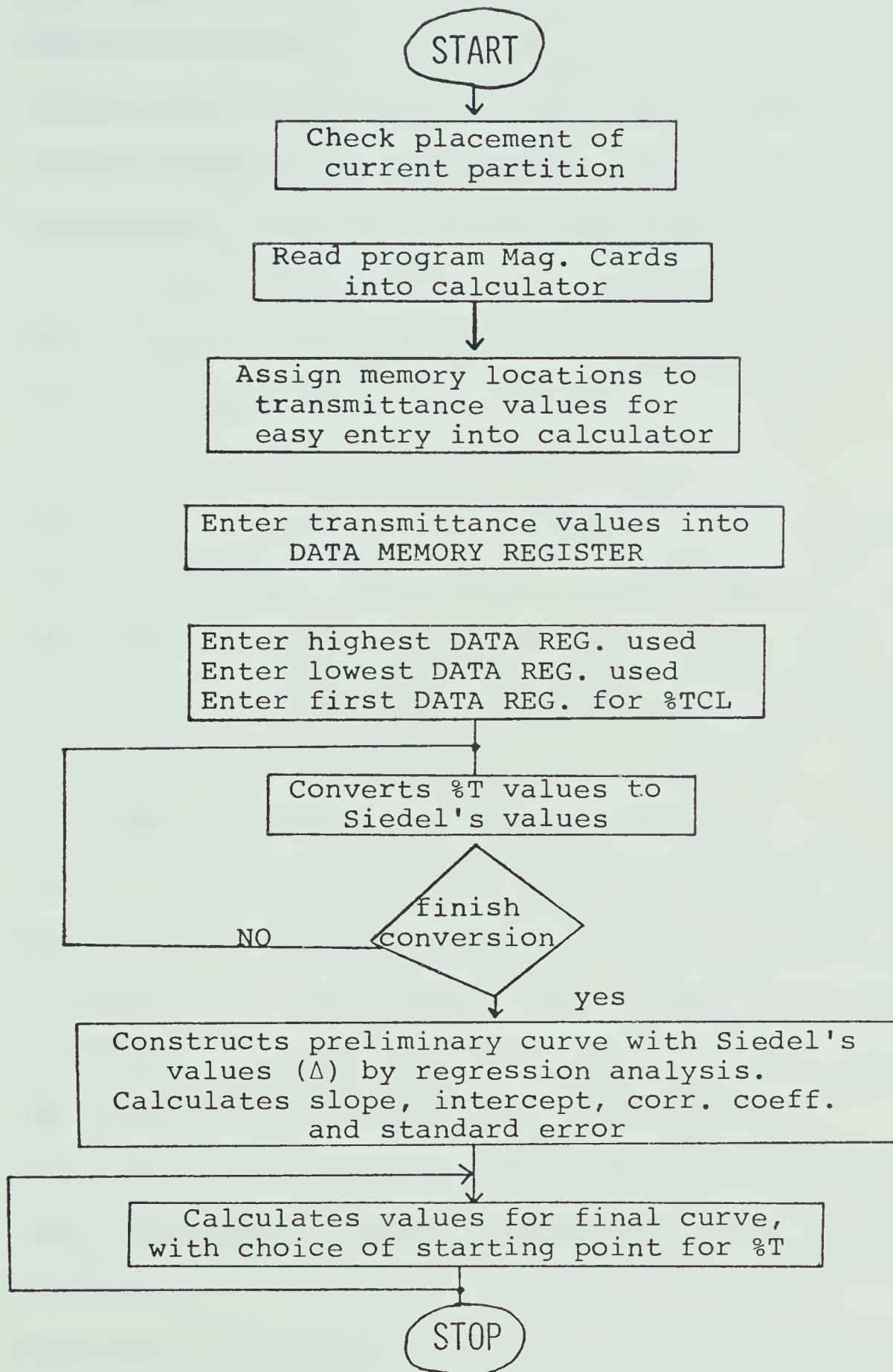


Figure 12. Flow chart diagram for calculator program.

for two seconds.

3. The preliminary curve of Δ clear vs Δ filtered is then constructed using the built-in linear regression analysis of the calculator. The display shows the DMR for Δ cleared as entered into the hardware statistics of the calculator. "1" in the display indicates completion of calculations.
4. The values for the equation of the preliminary curve are then obtained, that is

$$y = b + ax$$

where y is Δ clear, x is Δ filtered, b is the intercept and a the slope. (See note 8 on user instructions.)

5. Once the preliminary curve is constructed, the values for the final curve are then obtained. The starting point of %T for a relative intensity of 1 is entered. An option is given at this point to either choose the %T as low as 5% and obtain values higher than this or use the seven point system which includes setting 50%T - relative intensity of 0 and then obtain 3 values above 50%T and 3 values below 50%T. If the 7 step method is used, 50%% is entered and a flag is set (step 9 and 10).
6. The values of the final curve are then calculated and are displayed by pressing the Run/Stop button of the calculator.
7. Draw the final curve on a 2 by 2 log paper with %T ordinate and relative intensity abscissa (Fig. 3).

This program was used in almost all emulsion calibration done in this work especially the latter calibrations done for

quantitative analysis. The program was checked against another program written in Fortran II (46), that has been used earlier in our lab. The results obtained were in complete agreement.

The advantages of the calculator program include quick and easy entry of data with ease of changing and rechecking entered data (the data can be stored on magnetic cards); time sharing and cost involved in the use of computers are eliminated. Also the new program as compared to the Fortran II program incorporates an option in the calculation of the final curve.

After extensive use of the program it has been realized that the values of the equation that define the final emulsion calibration curve can be determined with the calculator, so that the two curves usually drawn when the calibration is done manually are completely omitted; with this capability the user only has to enter the transmittance of standards, samples and when necessary internal standard lines to obtain relative intensity values; a further extension of the program could also include determining the values of the equation that defines the working curve by least square fit. Since some analysts prefer to see their calibration curves and/or analytical curves on log log plots, these additional features could be added as options. A listing of the program with user instructions as listed on a T1 programmable form is shown below.

TITLE Calculation for Emulsion Calib. PAGE 1 OF EmulPROGRAMMER A. Bollo-Kamara DATE Jan. 28/78TI Programmable
Program Record Partitioning (Op 17) 4, 7, 9, 5, 9 Library Module None Printer x Cards 1
(Sides 1 & 2)


PROGRAM DESCRIPTION

Based on the two step filter method for a given set of DATA of Percent T filtered step and percent T cleared step:

- (a) Percent T is converted to siedel values.
- (b) Preliminary curve is done by linear regression analysis.
- (c) Final calibration curve is obtained by quadratic fit.
- (d) Very flexible in that choice of starting point for final curve is determined by the user.

USER INSTRUCTIONS

STEP	PROCEDURE	ENTER	PRESS	DISPLAY
1	Assign %T filtered step and %T cleared step to DATA Registers in decending order, i.e. RegN has first %T filt. step and least Data Reg. has the last %T cleared step value.			
2	Enter highest DATA Reg. used	Reg(N)	A	N
3	Enter lowest DATA Reg. used	RegN-Data	B	(N-DATA-1)
4	Enter first DATA Reg. used for %T cl.	REE-N(cl)	C	REENcl
5	Enter filter used	filt %	2nd A'	filt %
6	Convert to siedels value		D	RegN, siedel val.
	Conversion is completed			'1'
7	Construct Preliminary curve		E	(RegNcl) as entered
	Preliminary curve has been constructed			'1'
8	Equ. of Preliminary curve, intercept		R/S	intercept
	$y = b + ax$		R/S	slope
	$b = \text{intercept}$		R/S	Corr. Coeff.
	$a = \text{slope}$		R/S	std err.

USER DEFINED KEYS	DATA REGISTERS ()	LABELS (Op 08)
A ✓	0 Highest DATA Reg	10 Calib.
B ✓	1	11 Calib.
C ✓	2 Least square	12 Calib
D ✓	3 regression	
E ✓	4 analysis	
A' ✓	5	
B' ✓	6	
C' ✓	7 Count for R.I	
D' ✓	8 TRAM cl 1st Reg	
E' not used	9 Highest DATA Reg	
FLAGS / 0	1	2 3 4 5 6 7 8 9

TITLE Calculation for Emulsion Calib. PAGE 2 OF EmulPROGRAMMER A. Bollo-Kamara DATE Jan. 28/78TI Programmable
Program Record Partitioning (Op 17) [4,5,9,5,9] Library Module none Printer Cards

PROGRAM DESCRIPTION

Preliminary curve has been constructed.

- final curve is calculated
- an option is given: (1) set 50% T = Rel. Int. of 1
(2) use a low ZT value about 5%T = Rel. Int. of 1

Both methods have their advantages.

USER INSTRUCTIONS

STEP	PROCEDURE	ENTER	PRESS	DISPLAY
9	Enter starting point of ZT for Rel. Int. of 1, 50 or ?	<u>x</u>	2nd B	0
10	If 50% is used to this step otherwise OMIT.		2nd C'	0
11	Start calculation		2nd D'	
12	Record ZT			ZT
13	Record Rel. Int.		R/S	Rel. Int.
14	Repeat 13		R/S	ZT
15	Continue 14 pressing R/S until '1' is on display		R/S	Rel. Int.
16	Draw final curve by hand. Repeat steps 8 to 15 for different starting points of ZT.			'1'

USER DEFINED KEYS		DATA REGISTERS (<u>mv</u> <u>LEV</u>)				LABELS (Op 08)				
A		0		0		[mv] [1/x] [CE] [CLR] [RST] [x ²]				
B		1		1		[C] [1/x] [STO] [RC] [SUM] [y ⁿ]				
C		2		2		[EE] [1] [1] [+] [COT] [X]				
D		3		3		[SQR] [] [RST] [+] [R/S] []				
E		4		4		[x/y] [=] [ON] [OFF] [] []				
A'		5		5		[] ✓ [] ✓ [] ✓ [] ✓ [] ✓ []				
B'		6		6		[] [] [] [] [] []				
C		7		7		[] [] [] [] [] []				
D		8		8		[] [] [] [] [] []				
E		9		9		[] [] [] [] [] []				
FLAGS ✓ 0		1	2	3	4	5	6	7	8	9

TITLE Emulsion CalibrationPAGE 1 OF EmulPROGRAMMER A. Bollo-KamaraDATE Jan. 28/78TI Programmable
Coding Form 

LOC	CODE	KEY	COMMENTS	LOC	CODE	KEY	COMMENTS	LOC	CODE	KEY	COMMENTS
70		2nd LbL	Store data	43	RC1		clears T	69	2nd OP		intercept
11	A		Register	59	59		register	12	12		
42	STO		(Highest	32	x=t			91	R/S		
0	0		used)	43	RC1			32	x t		slope
91	RYS			0	0			91	R/S		
76	2nd LbL			6	66	2nd Pause		69	2nd OP		
12	B		Store	22	INV		test if all	13	13		
42	STO		lowest data	67	x=t		reg has	91	R/S		
59	59		register	38	2nd SIN		been tre-	53	C		
53	C		used	25	CLR		ated	53	C		
43	RC1		DSZ is	32	x=t		if yes	43	RC1		
59	59		used before	69	2nd OP		displays 1	2	2		
75	-		loop (-)	10	IO			75	-		
1	1			22	INV			53	C		
54)			58	2nd fix			53	C		
42	STO			7	91	R/S		69	2nd OP		
59	59			76	2nd LbL		Linear re-	12	12		
91	R/S			15	E		gression	54)		
76	2nd LbL			36	2nd PAM		analysis	65	x		
13	C		Highest	1	1		starts	43	RC1		
42	STO		data Reg.	71	SBR			13	1		calculates
8	8		for TRANS	25	CLR			54)		Std
91	R/S		clear	76	2nd LbL		clears reg	75	-		error
76	2nd LbL			39	COS		01 06	53	C		
14	D		Transfers	73	RCL2ndInd		In. address	53	C		
43	RC1		highest	8	8		enters	32	x=t		
0	0		data Reg.	32	x=t			54)		
42	STO		for L.R.A.	69	2nd OP		decrease	65	x		
9	9		and	38	38		reg 8 by 1	43	RC1		
76	2nd LbL		Label Cal-	73	RC12ndInd			6	6		
38	2nd sin		culates	9	a			14	54)	
53	C		siedels	78	2nd Σ +		Enters Y	54)		
53	C		function	69	2nd OP		decrease reg	54)		
1	1			39	39		9 by 1	55	÷		
0	0			29	2nd CP			53	C		
0	0			53	C			43	RC1		
55				43	RC1			3	3		
73	RC1 Ind		Indirect	59	59			75	-		
0	0		Address	54)			2	2		
54)			32	x=t			54)		
75	-			43	RC1			15	54)	
1	1			8	8			50	1x1		
54)			66	2nd Pause			34	\sqrt{x}		
28	2nd Log			22	INV		Test if all	91	R/S		
58	2nd fix		3 decimal	67	2nd x=t		data has	76	2nd LbL		
3	3		place	39	2nd COS		been en-	16	A'		
66	2nd Pause		2 sec	25	CLR		tered	42	STO		Stores bet-
66	2nd Pause		delay	32	x t			10	10		ter in Reg
66	2nd Pause		pause	69	2nd OP			91	R/S		10
66	2nd Pause			10	IO			76	2nd LbL		
5	63	2nd Ex Ind	Stores	22	INV			MERGED CODES			
0	0		siedels val-	58	2nd fix			62	STO	72	STO
69	2nd OP		ue in RegN	91	R/S			63	RC1	73	RC1
30	30		Dec. RegN	58	2nd fix			64	2nd	74	2nd
29	2nd Cp		by 1	4	4			TEXAS INSTRUMENTS			

TITLE Emulsion Calibration PAGE 2 OF EmulPROGRAMMER A. Bollo-KamaraDATE Jan. 28/78TI Programmable
Coding Form 

LOC	CODE	KEY	COMMENTS	LOC	CODE	KEY	COMMENTS	LOC	CODE	KEY	COMMENTS
16	17	B'		21	58	58		27	0	0	
	42	STO	Starting		53	C			55	÷	
	67	56	ZT for RI=1		1	1			43	RC1	
	58	EXC			0	0			11	11	
	11	11			0	0			54)	
	91	R/S	set flag	22	55	÷			75	-	
	76	2nd Lbl	0		53	C	converts		1	1	
	18	C'			43	RC1	Siedel's		54)	
	86	St fla			58	58	to ZT.		28	2nd Log	
	0	0			22	inv			58	2nd fix	
	91	R/S			28	2nd Log			3	3	
	76	2nd Lbl			85	+			69	2nd OP	
	19	D'			1	1			15	15	
	0	0			54)			42	STO	
	48	EXC			54)			13	13	
	7	7		23	91	R/S			53	C	
	53	C	calculates		42	STO			1	1	
	43	RC1	rel. Int-		56	56			0	0	
	10	10	ensity from		69	2nd OP	calculates		0	0	calculates
	55	÷	filter		27	27	Rel. Int.		58	÷	Rel. Int.
19	1	1	value		53	C		29	53	C	for ZT.
	0	0			43	RC1			43	RC1	
	0	0			10	10			13	inv	
	54)			45	x			22	2nd Log	
	58	2nd fix			43	RC1			28	+	
	3	3		24	7	7			85	1	
	52	STO			54)			1)	
	10	10			91	R/S			54)	
	48	EXC			9	9			54	R/S	
	12	12			9	9	Test if		91	STO	
	43	RC1			32	x ≥ t	ZT > 99%	30	42	11	
	56	56			43	RC1			11	2nd OP	
	91	R/S			56	56			69	27	
	1	1			22	inv			27	C	
	91	R/S			77	x ≥ t			53	C	
	76	2nd Lbl		25	30	TAN			53	RC1	
	30	TAN			87	If fla	test flago		43	12	
	53	C	converts		0	0			12	y ^s	
	53	C	ZT=RI,1		37	p + R			45	RC1	
	1	1	to Siedels		69	2nd OP			43	7	
	0	0	value		10	10		31	7		
	0	0			22	inv			54)	
	55	÷			58	2nd fix			35	1/x	
	43	RC1			91	R/S			54)	
	56	56		26	76	2nd Lbl			91	R/S	
	54)			37	P R			21	2nd OP	
	75	-			0	0			1	1	
	1	1			48	EXC			32	x y	
	54)			7	7			43	RC1	
	28	2nd Log			76	2nd Lbl		31	11	11	
21	58	2nd fix			36	PGM		MERGED CODES			
	3	3			53	C		62	STO	83	GTN
	69	2nd OP			53	C		63	RC1	84	RC1
	14	14			1	1		64	2nd OP	92	INV
	42	STO			0	0		72	STO		
								73	RC1		
								74	2nd OP		

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